LWT - Food Science and Technology 63 (2015) 620–625

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Evaluation of oil content and fatty acid composition in the seed of grapevine varieties

Jaromír Lachman [a, *], Alena Hejtmánková [a], Jan Táborský [a], Zora Kotíková [a], Vladimír Pivec [a], Radomíra Střalková [b], Alena Vollmannová [c], Tatiana Bojňanská [d], Martin Dědina [e]

[a] Department of Chemistry, Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences Prague, Kamýcká 129, 165 21 Prague 6-Suchdol, Czech Republic
[b] Viticulture Research Station (Karlštejn), Crop Research Institute, Drnovská 507, 161 06 Prague 6-Ruzyně, Czech Republic
[c] Department of Chemistry, Faculty of Biotechnology and Food Sciences, Slovak University of Agriculture in Nitra, Tr. A. Hlinku 2, 949 76 Nitra, Slovak Republic
[d] Department of Storing and Processing Plant Products, Faculty of Biotechnology and Food Sciences, Slovak University of Agriculture in Nitra, Tr. A. Hlinku 2, 949 76 Nitra, Slovak Republic
[e] Research Institute of Agricultural Engineering Prague, Drnovská 507, 161 06 Prague 6-Ruzyně, Czech Republic

A R T I C L E I N F O

Article history:
Received 10 July 2014
Received in revised form
12 March 2015
Accepted 13 March 2015
Available online 20 March 2015

Keywords:
Grape seeds
Grapevine varieties
Oil content
Fatty acid profiles
Effect of variety and year

A B S T R A C T

From the gene collection of the Viticulture Research Station Karlštejn samples of seeds of selected grapevine varieties were obtained during the harvest of 2011 and 2012. Average oil content in analysed grapevine varieties in 2011 was 11.60 ± 0.33 g/100 g seed dry matter. Linoleic acid was the most abundant fatty acid in all analysed grape seed oils, contributing between 68.10 g/100 g oil and 78.18 g/100 g oil. Linolenic acid was present only in small trace quantities ranging from 0.29 g/100 g to 0.77 g/100 g oil. Oleic acid content conformed to MUFA content, which ranged from 8.82 g/100 g–16.92 g/100 g. SFA ranged between 9.04 g/100 g and 12.82 g/100 g of TFA. Statistical analysis revealed close correlation between PUFA and linoleic acid ($R^2 = 0.998$) and MUFA and oleic acid content ($R^2 = 0.994$). Variety of cultivation showed significant impact on the content of fatty acids in oil. Principal component analysis revealed differences or similarity of analysed grapevine varieties related to the content of major FA. The year of cultivation showed different effect on individual FA content.

1. Introduction

Grapes are one of the major fruit crops and about eighty percent of the harvest is used by the winemaking industry, which leads to the generation of large quantities of seed by-product (Yi et al., 2009). Grape seed oil has a large scale of application, being used in various fields from cosmetics to cooking. Grape seed oil is gaining popularity as culinary oil, and has been studied as a possible source of specialty lipids (Bail, Stuebiger, Krist, Unterweger, & Buchbauer, 2008). It is a rich source of linoleic acid (Beveridge, Girard, Kopp, & Drover, 2005), which is associated with promotion of cardiovascular health by down-regulating low-density lipoprotein cholesterol. Grape-seed oils have emerged as a product with potential to be used in food and pharmaceutical applications (Crews et al., 2006). The benefits of grapes are associated with polyunsaturated fatty acids (PUFA) present mostly in seeds. Grape-seed oils may be a good option, as numerous benefits associated with their composition were reported, mainly in terms of essentials fatty acids and vitamin E. Polyunsaturated acids such as linoleic and linolenic acids are essential for the human metabolism due to the lack of enzymes responsible for their biosynthesis (Hanganu, Todaşcă, Chira, Maganu, & Roşca, 2012). PUFA are considered desirable compounds in the human diet because of their effect in reducing the incidence of cardiovascular disease and cancer (Yi et al., 2009). According to Bellido et al. (2006), the ingestion of oleic acid is related to the reduction of the level of low density lipoproteins and consequently, the prevention of arteriosclerosis. Due to dietetic habits, increased consumption of n-3 acids has been

Abbreviations: FA, fatty acids; SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids; TFA, total fatty acids.

* Corresponding author. Tel.: +420 224382717; fax: +420 234381840.
E-mail address: lachman@af.czu.cz (J. Lachman).

http://dx.doi.org/10.1016/j.lwt.2015.03.044
0023-6438/

recommended in the diet (Gebauer, Harris, Kris-Etherton, & Etherton, 2005).

Grape seeds contain about 14–17 g/100 g oil and the main interest in grape seed oil lies in its high content of unsaturated acids, which exceeds those in safflower, sunflower and corn oil (Cao & Ito, 2003). Grape seed oil consists mainly of triglycerides, which are rich in monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA), compared to other oil-rich seeds (Baydar & Akkurt, 2001). The oil contents were found to be different for each variety. Saturated fatty acids contents were lower than the values of MUFA and PUFA in all genotypes. Among the identified fatty acids, linoleic acid (C18:2) was the predominant fatty acid and it was followed by oleic acid (C18:1) and palmitic acid (C16:0) in all varieties (Tangolar, Ozoğul, Tangolar, & Torun, 2009).

According to present knowledge, no study has been performed until now that focused on the potential use of seed oils of grape varieties grown in the Czech Republic. As a part of ongoing efforts to develop value-added utilisations of fruit seeds, this study was conducted to determine grape seed oils yield. In this research, the seeds of wine grape and table grape varieties were examined for oil content. Moreover, the FA compositions of oils of these seed samples were determined with the aim of evaluation of the fatty acid profile and the effect of year of harvest on fatty acid content.

2. Material and methods

2.1. Plant material

In total, 23 samples of grape seeds from the gene collection of the Viticulture Research Station Karlštejn, Czech Republic, of selected varieties of grapes were obtained during the harvest of 2011 and 2012 for comparison of the effect of the year (Tables 1 and 2) and additionally 18 other varieties in 2011 (Table 3) for the evaluation of FA content in individual varieties. All seeds were, after pressing, manually separated from the skins in an average of 10 kg samples of grapes and dried to a constant weight. No seeds passed through the wine-making process. Oil concentrations in 2011 are shown in Fig. 1.

2.2. Chemicals

Methanol p.a. (Lach-Ner Ltd., Neratovice, Czech Republic); methanolic base 0.5 mol/L (Supelco, Sigma–Aldrich CZ, Prague, Czech Republic); GC grade hexane (Lach-Ner Ltd., Neratovice, Czech Republic); sodium chloride p.a. (Lach-Ner Ltd, Neratovice, Czech Republic); distilled water.

2.3. Determination of oil content by Soxhlet method

A Soxhlet apparatus was used for the extraction of oil from the dried powdered seeds. Finely powdered grape seeds in an HR 2185 Philips electric mill (Philips, Ltd., Amsterdam, the Netherlands) (ca 0.5 g) were extracted with hexane (p.a., Lach-Ner Ltd, Neratovice, Czech Republic) at 70 °C, then hexane was removed on a Büchi rotovapor R-215 (Büchi Labortechnik GmbH, Essen, Germany) at 65 °C and grape oil was then further dried to a constant weight in an oven at 60 °C and weighed. Oil contents were expressed per dry weight of the seeds (w/w).

2.4. Determination of fatty acids in grape oils with GC-FID

2.4.1. Preparation of methyl esters

40 μL of the oil sample was pipetted to a thick-walled tube (10 × 1.5 cm), suitable for use in a centrifuge, with an automatic pipette. 0.5 mL of methanol and 0.5 mL of methanolic base (sodium methanolate) was added to this tube. The tube was carefully sealed and the content at the bottom of the tube was gently shaken. After shaking, the tube was placed in a water bath at 75–80 °C and the mixture was allowed to react for 1 min. After this time, the tube was taken out and the content shaken gently again for better dispersion

Table 1
Composition of major and essential fatty acids in grape seeds of vine varieties in 2011 and 2012 (g/100 g oil).

Variety	Palmitic acid			Stearic acid			Oleic acid			Linoleic acid			α-Linolenic acid		
	2011	2012	mean ± SD	2011	2012	mean ± SD	2011	2012	mean ± SD	2011	2012	mean ± SD	2011	2012	mean ± SD
André (B)	7.14	7.20	7.17 ± 0.04	3.18	3.40	3.29 ± 0.16	12.98	15.01	14.00 ± 1.44	74.24	72.03	73.14 ± 1.56	0.33	0.28	0.31 ± 0.04
Bacchus (W)	7.08	7.58	7.33 ± 0.35	3.39	3.11	3.25 ± 0.20	13.36	11.63	12.50 ± 1.22	73.43	75.44	74.44 ± 1.42	0.31	0.42	0.37 ± 0.08
Pinot N. Précoce (B)	6.91	6.60	6.76 ± 0.22	4.57	4.44	4.51 ± 0.09	12.76	12.91	12.84 ± 0.11	71.90	73.55	72.73 ± 1.17	0.54	0.46	0.50 ± 0.06
Děvín (W)	5.94	5.98	5.96 ± 0.03	5.24	4.83	5.04 ± 0.29	15.11	14.59	14.85 ± 0.37	71.25	72.60	71.93 ± 0.96	0.49	0.38	0.44 ± 0.08
Chardonnay (W)	6.44	6.50	6.47 ± 0.04	5.65	3.81	4.73 ± 1.30	16.78	16.52	16.65 ± 0.18	69.25	71.12	70.19 ± 1.32	0.36	0.32	0.34 ± 0.03
Kerner (W)	6.40	6.62	6.51 ± 0.16	3.85	3.71	3.78 ± 0.10	12.95	14.45	13.70 ± 1.06	74.61	72.75	73.68 ± 1.32	0.42	0.37	0.40 ± 0.04
Madeleine Ang. (W)	6.56	6.82	6.69 ± 0.18	4.96	4.51	4.74 ± 0.32	13.10	13.30	13.20 ± 0.14	72.60	72.81	72.71 ± 0.15	0.47	0.33	0.40 ± 0.10
Pinot Meunier (B)	6.72	7.07	6.90 ± 0.25	3.71	3.45	3.58 ± 0.18	13.56	14.69	14.13 ± 0.80	73.67	72.54	73.11 ± 0.80	0.39	0.39	0.39 ± 0.00
Muscat Dessert. (W)	6.81	7.02	6.92 ± 0.15	4.05	4.01	4.03 ± 0.03	12.86	14.54	13.70 ± 1.19	73.73	72.43	73.08 ± 0.92	0.37	0.37	0.37 ± 0.00
Pálava (R)	6.43	6.62	6.53 ± 0.13	3.66	4.14	3.90 ± 0.34	10.42	13.95	12.19 ± 2.50	77.23	73.37	75.30 ± 2.73	0.44	0.40	0.42 ± 0.03
Veltliner Green (W)	6.76	6.89	6.83 ± 0.09	3.68	3.42	3.55 ± 0.18	9.97	10.49	10.23 ± 0.37	77.19	77.08	77.14 ± 0.08	0.62	0.48	0.55 ± 0.10
Zenit (W)	7.83	7.28	7.56 ± 0.39	4.24	3.74	3.99 ± 0.35	12.58	14.70	13.64 ± 1.50	71.64	71.78	71.71 ± 0.10	0.77	0.45	0.61 ± 0.23
Pinot N. Swiss (B)	6.78	7.39	7.09 ± 0.43	3.63	4.06	3.85 ± 0.30	12.93	16.06	14.50 ± 2.21	74.37	69.85	72.11 ± 3.20	0.43	0.37	0.40 ± 0.04
Pinot Noir (B)	6.84	6.89	6.87 ± 0.04	4.05	3.96	4.01 ± 0.06	13.43	15.79	14.61 ± 1.67	73.55	71.37	72.46 ± 1.54	0.38	0.32	0.35 ± 0.04
Pinot Blanc (W)	6.33	6.12	6.23 ± 0.15	3.58	3.45	3.52 ± 0.09	15.88	18.00	16.94 ± 1.50	71.80	70.31	71.06 ± 1.05	0.37	0.32	0.35 ± 0.04
Arom. Riesling (W)	7.14	6.35	6.75 ± 0.56	3.18	3.22	3.20 ± 0.03	12.98	15.92	14.45 ± 2.08	74.24	72.50	73.37 ± 1.23	0.33	0.34	0.34 ± 0.01
Riesling Red (R)	6.68	6.90	6.79 ± 0.16	3.21	3.28	3.25 ± 0.05	13.62	13.57	13.60 ± 0.04	73.95	74.17	74.06 ± 0.16	0.50	0.43	0.47 ± 0.05
Rheinriesling (W)	6.42	6.96	6.69 ± 0.38	3.29	3.67	3.48 ± 0.27	14.13	14.54	14.34 ± 0.29	74.02	72.85	73.44 ± 0.83	0.46	0.39	0.43 ± 0.05
Riesling Italian (W)	6.34	5.98	6.16 ± 0.25	5.25	4.58	4.92 ± 0.47	16.26	15.91	16.09 ± 0.25	69.95	71.28	70.62 ± 0.94	0.41	0.39	0.40 ± 0.01
Sauvignon (W)	6.39	6.63	6.51 ± 0.17	5.51	6.20	5.86 ± 0.49	11.08	12.28	11.68 ± 0.85	75.02	73.07	74.05 ± 1.38	0.40	0.38	0.39 ± 0.01
Siegerrebe (B/R)	6.21	6.08	6.15 ± 0.09	4.61	5.00	4.81 ± 0.28	10.59	12.21	11.40 ± 1.14	74.97	74.37	74.67 ± 0.42	0.63	0.44	0.54 ± 0.13
Silvaner Green (W)	8.02	8.34	8.18 ± 0.23	3.85	4.30	4.08 ± 0.32	13.12	13.02	13.07 ± 0.07	72.79	72.16	72.48 ± 0.45	0.49	0.43	0.46 ± 0.04
Záhoranka (W)	6.13	6.21	6.17 ± 0.06	3.66	3.77	3.72 ± 0.08	11.24	11.49	11.37 ± 0.18	76.90	76.54	76.72 ± 0.26	0.41	0.37	0.39 ± 0.03
Average	**6.76**[a]	**6.85**[b]	**6.81 ± 0.59**	**4.10**[a]	**3.97**[a]	**4.04 ± 0.74**	**13.14**[a]	**14.12**[b]	**13.63 ± 1.73**	**73.43**[a]	**72.87**[b]	**73.15 ± 1.94**	**0.45**[a]	**0.38**[b]	**0.42 ± 0.08**

Pinot N. Précoce = Pinot Noir Précoce; Madeleine Ang. = Madeleine Angevine; Muscat Dessert. = Muscat Dessertnyi; Pinot N. Swiss = Pinot Noir Swiss selection; Arom. Riesling = Aromatic Riesling; B = blue; W = white; R = rose; values marked with different letters in columns are significantly different at $P \leq 0.05$. All analyses were carried out in three replicates.

Table 2
Composition of individual species of fatty acids and n-3/n-6 fatty acids ratio in grape seeds of vine varieties in 2011 and 2012 (g/100 g oil).

Variety	SFA			MUFA			PUFA			*trans*-FA			n-3/n-6		
	2011	2012	mean ± SD	2011	2012	mean ± SD	2011	2012	mean ± SD	2011	2012	mean ± SD	2011	2012	mean ± SD
André	10.67	10.93	10.80 ± 0.18	13.22	15.21	14.22 ± 1.41	74.74	72.41	73.58 ± 1.65	0.03	0.03	0.03 ± 0.00	225	257	241 ± 22.6
Bacchus	10.84	10.98	10.91 ± 0.10	13.58	11.77	12.68 ± 1.28	73.85	75.98	74.92 ± 1.51	0.04	0.03	0.04 ± 0.01	237	180	209 ± 40.3
Pinot N. Précoce	12.07	11.48	11.78 ± 0.42	12.91	13.07	12.99 ± 0.11	72.65	74.23	73.44 ± 1.12	0.07	0.03	0.05 ± 0.03	133	160	147 ± 19.1
Děvín	11.60	11.18	11.39 ± 0.30	15.24	14.70	14.97 ± 0.38	71.85	73.10	72.48 ± 0.88	0.03	0.03	0.03 ± 0.00	145	191	168 ± 32.5
Chardonnay	12.51	10.64	11.58 ± 1.32	16.92	16.68	16.80 ± 0.17	69.68	71.55	70.62 ± 1.32	0.03	0.03	0.03 ± 0.00	192	222	207 ± 21.2
Kerner	10.63	10.67	10.65 ± 0.03	13.05	14.56	13.81 ± 1.07	75.19	73.20	74.20 ± 0.02	0.03	0.04	0.04 ± 0.01	178	197	188 ± 13.4
Madeleine Angevine	12.05	11.72	11.89 ± 0.23	13.22	13.43	13.33 ± 0.15	73.31	73.28	73.30 ± 0.02	0.03	0.04	0.04 ± 0.01	154	221	188 ± 47.4
Pinot Meunier	10.77	10.85	10.81 ± 0.06	13.78	14.89	14.34 ± 0.79	74.23	73.07	76.65 ± 0.82	0.03	0.03	0.03 ± 0.00	189	186	188 ± 2.1
Muscat Dessertnyi	11.25	11.36	11.31 ± 0.08	13.14	14.68	13.91 ± 1.09	74.29	72.89	73.59 ± 0.99	0.04	0.03	0.04 ± 0.01	199	196	198 ± 2.1
Pálava	10.43	11.07	10.75 ± 0.45	10.52	14.06	12.29 ± 2.50	77.78	73.86	75.82 ± 2.77	0.03	0.03	0.03 ± 0.00	176	183	180 ± 5.0
Veltliner Green	10.81	10.62	10.72 ± 0.13	10.10	10.61	10.36 ± 0.36	77.95	77.65	77.80 ± 0.21	0.03	0.03	0.03 ± 0.00	125	161	143 ± 25.5
Zenit	12.76	11.43	12.10 ± 0.94	12.77	14.88	13.83 ± 1.49	72.67	72.41	72.54 ± 0.18	0.04	0.03	0.04 ± 0.01	93	160	127 ± 47.4
Pinot N. Swiss	10.77	11.82	11.29 ± 0.74	13.25	16.26	14.75 ± 2.13	74.94	70.32	72.63 ± 3.27	0.03	0.03	0.03 ± 0.00	173	189	181 ± 11.3
Pinot Noir	11.24	11.18	11.21 ± 0.04	13.57	15.97	14.77 ± 1.70	74.11	71.80	72.96 ± 1.63	0.03	0.03	0.03 ± 0.00	194	223	209 ± 20.5
Pinot Blanc	10.28	9.90	10.09 ± 0.27	16.05	18.17	17.11 ± 1.50	72.23	70.73	71.48 ± 1.06	0.03	0.03	0.03 ± 0.00	194	220	207 ± 18.4
Aromatic Riesling	10.67	9.83	10.25 ± 0.59	13.21	16.08	14.65 ± 2.03	74.74	72.97	73.86 ± 1.25	0.03	0.03	0.03 ± 0.00	225	213	219 ± 8.5
Riesling Red	10.25	10.50	10.38 ± 0.18	13.74	13.68	13.71 ± 0.04	74.55	74.70	74.63 ± 0.11	0.03	0.03	0.03 ± 0.00	148	172	160 ± 17.0
Rheinriesling	10.04	10.94	10.49 ± 0.64	14.23	14.65	14.44 ± 0.30	74.61	73.35	73.98 ± 0.89	0.03	0.03	0.03 ± 0.00	161	187	174 ± 18.4
Riesling Italian	11.96	10.92	1.44 ± 0.74	16.42	16.05	16.24 ± 0.26	70.47	71.75	71.11 ± 0.91	0.03	0.03	0.03 ± 0.00	171	183	177 ± 8.5
Sauvignon	12.31	13.23	12.77 ± 0.65	11.20	12.39	11.80 ± 0.84	75.55	73.56	74.56 ± 1.41	0.04	0.03	0.04 ± 0.01	188	192	190 ± 2.8
Siegerrebe	11.43	11.48	11.46 ± 0.04	10.74	12.34	11.54 ± 1.13	75.95	75.02	75.49 ± 0.66	0.04	0.03	0.04 ± 0.01	119	169	144 ± 35.4
Silvaner Green	12.23	13.01	12.62 ± 0.55	13.27	13.18	13.23 ± 0.06	73.39	72.71	73.05 ± 0.48	0.02	0.03	0.03 ± 0.01	149	168	159 ± 13.4
Záhoranka	10.13	10.32	10.23 ± 0.13	11.32	11.61	11.47 ± 0.21	77.49	77.04	77.27 ± 0.32	0.03	0.03	0.03 ± 0.00	188	207	198 ± 13.4
Average	**11.27**[a]	**11.16**[a]	**11.22 ± 0.80**	**13.30**[a]	**14.27**[a]	**13.79 ± 1.64**	**74.04**[a]	**73.37**[a]	**73.71 ± 1.78**	**0.03**[a]	**0.03**[a]	**0.03 ± 0.01**	**172**	**193**	**182 ± 19.0**

Pinot N. Précoce = Pinot Noir Précoce; Pinot N. Swiss = Pinot Noir Swiss selection. [a] SFA, MUFA and PUFA in 2011 and 2012 were not significantly different at $P \leq 0.05$. All analyses were carried out in three replicates.

of the fat particles. Thereafter, the tube was again placed in a water bath for further 3 min. When after this period the solution appeared clear, the tube was removed and the content cooled rapidly under cold running water. If the content is not clear, the tube was left in a water bath for an additional 1 min. After cooling, 1.5 mL of hexane was added to the reaction mixture and the entire volume of the tube was vigorously shaken. Furthermore, 5 mL of saturated aqueous NaCl solution was added and the content was again vigorously shaken. The tube was placed in a centrifuge EBA 20 (Hettich-Zentrifugen GmbH & Co. KG, Tuttlingen, Germany), which was set at 3000 g for 5 min. After this time, the tube was removed from the centrifuge and, using an automatic pipette, 800 µL of the upper organic phase was collected into a dark vial of 1.5 mL volume. If GC analysis had not taken place immediately after the preparation of the methyl esters, the vial was stored in a refrigerator, and analysis was carried out by the next day.

2.4.2. Gas chromatography with flame ionization detector (GC-FID)

For the determination of fatty acids a little modified method of Simionato et al. (2010) was used. For analysis of the samples an Agilent 7890 gas chromatograph equipped with an autosampler G4513A and a flame ionization detector (FID) (Agilent Technologies, Inc., Wilmington, USA), quartz capillary column SP -2560, 100 m × 0.25 µm (film thickness 0.2 µm) (Sigma–Aldrich Inc., LLC, St. Louis, USA), were applied.

Used gases: carrier gas He of a purity 5.6; make-up N_2 with a purity of 6.0; gas flow in the detector N_2 25 mL/min; H_2 30 mL/min with purity 6.0; air 400 mL/min with purity of 5.0. Conditions of analysis: inlet pressure of the carrier gas 310.264 kPa (45 psi); split ratio 1:100; sprayed sample volume 1 µL; injector temperature 280 °C; detector temperature 280 °C; initial column temperature 140 °C for 5 min; temperature increase 4 °C/min; the upper isotherm 249 °C for 20 min; total analysis time 52.25 min.

Table 3
Composition of major and essential fatty acids in grape seeds of vine varieties available only in 2011 (g/100 g oil).

Variety	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid	α-Linolenic acid	SFA	MUFA	PUFA	*trans*-FA	n-3/n-6
Dornfelder (B)	7.91	3.66	13.09	71.43	0.42	11.99	13.31	72.09	0.15	170
Dětskij Rannij (B/R)	5.31	3.40	15.26	73.97	0.32	9.04	15.37	74.48	0.03	231
Bratislava White (W)	7.72	3.84	12.50	73.46	0.59	11.94	12.73	74.15	0.03	125
Auxerrois (W)	4.93	3.30	10.37	76.05	0.46	9.67	12.59	76.62	0.03	165
M. F. Lesseps (W)	5.91	3.52	15.41	72.92	0.44	9.78	15.52	73.51	0.03	166
Jacobsteiner (W)	7.09	3.82	11.64	75.24	0.43	11.23	11.76	75.74	0.03	175
Jaeger (W)	6.63	3.22	14.17	73.79	0.45	10.18	14.27	74.37	0.03	164
Muscat Early (W)	6.58	2.91	10.05	76.58	0.52	10.35	10.17	77.25	0.04	147
Zweigeltrebe (B)	7.09	3.38	13.37	73.75	0.34	10.82	13.59	74.22	0.03	217
Muscat Morav. (W)	7.89	4.46	13.56	70.00	0.45	12.82	13.81	70.63	0.04	156
Blue Portugal (B)	7.34	4.07	13.32	72.63	0.45	11.83	13.50	73.35	0.03	161
Müller Thurgau (W)	7.16	3.12	11.50	74.74	0.45	10.74	11.66	75.39	0.05	166
Silvaner Early (W)	8.00	4.18	12.66	72.89	0.47	12.54	12.83	73.48	0.03	155
Muscat Oberlin (W)	6.92	3.45	12.78	74.34	0.38	10.73	13.07	74.90	0.03	196
Veltliner Red (B/R)	7.28	3.94	13.01	73.29	0.47	11.65	13.12	73.91	0.03	156
Mathias János (W)	7.43	4.74	15.80	68.10	0.29	12.59	15.96	68.61	0.05	235
Basilicum (W)	7.16	4.59	11.33	72.72	0.48	12.20	11.49	73.62	0.06	152
Aurora (W)	6.36	3.64	8.67	78.18	0.52	11.37	8.82	79.01	0.04	150

M. F. Lesseps = Muscat Ferdinand Lesseps; Muscat Morav. = Muscat Moravian; B = blue; W = white; R = rose. All analyses were carried out in three replicates.

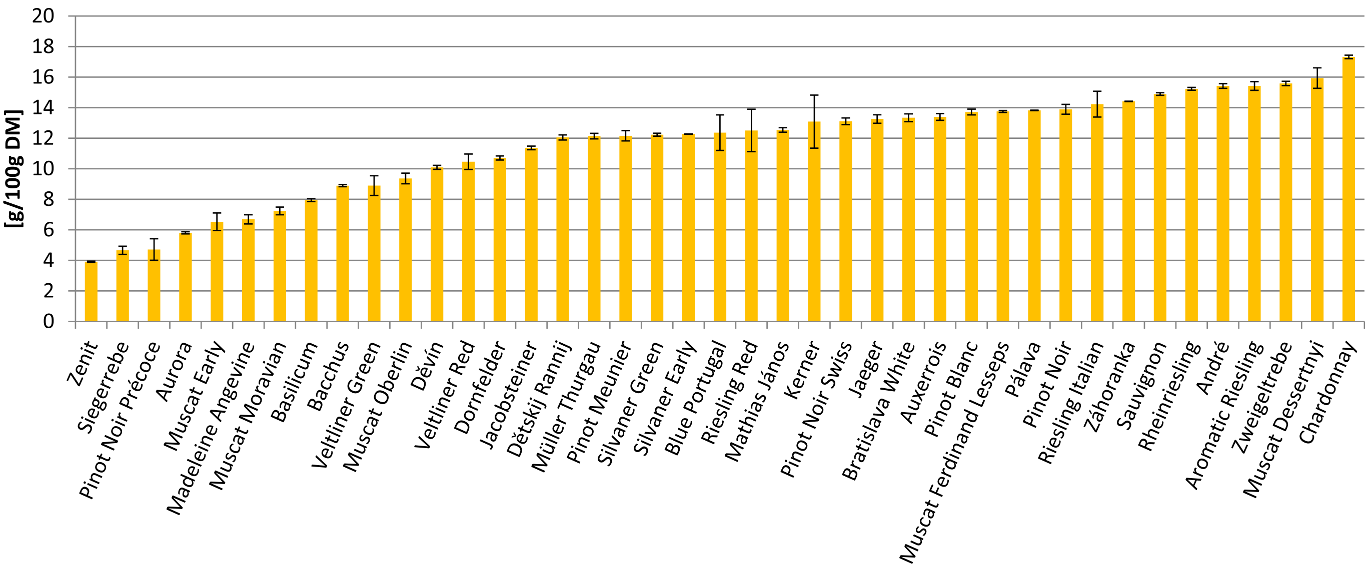

Fig. 1. Oil content in g/100 g in grape seeds of vine varieties in 2011 (content of oil is given in dry weight of the seeds).

ChemStation chromatographic software (Agilent Technologies Inc., Colorado Springs, USA), was used for evaluation of chromatograms. Compounds were identified by comparing the retention times of the analysed compounds with retention times of standards. Quantitative analysis was performed by the method of internal normalization. Areas of all peaks (excluding solvents) were summed, which was equal to the hundred percentage. Areas of the peaks correspond to the percentage composition of individual fatty acids in the oil. Parallel determinations were carried out in triplicates.

Intervals of limit of detection (LOD) for individual fatty acids were 0.08, 0.05, 0.09, 0.07 and 0.05 μg/mL for palmitic, stearic, oleic, linoleic and linolenic acid, respectively. The respective limits of quantification (LOQ) were 0.18, 0.12, 0.20, 0.19 and 0.14 μg/mL. Oleic acid and palmitic acid obtained the highest values for LOD and LOQ, while the lowest values for both limits were obtained by stearic, linoleic and linolenic acid.

2.5. Statistical analysis

Differences between mean values were evaluated by Tukey's test and t-test in the SAS computer program, version 9.1.3. (SAS Institute Inc., Cary, NC, USA) at the level of significance $P \leq 0.05$.

The principal component analysis (PCA) was used to reduce this complex data set to a lower dimension and reveal simplified structures and relation between individual wine grape varieties. In the assessment of differences among the varieties the dominant acids namely linoleic, palmitic, stearic and oleic acid have been included. The principle of this nonparametric method is based on re-expression data set as linear combination of its independent variables (so named principal components) having no correlation each other. In particular, the measurement of the variance along each principal component provides a means for comparison of relative importance of each considered dimension. In our calculation, the code written for Matlab R2014a (The Mathworks, Inc., Natick, Massachusetts, USA) was performed, based on single value decomposition algorithm. The related properties of individual grape varieties were then sorted (grouped) after their scores in the biplot graph (Fig. 2).

3. Results and discussion

3.1. Content of oil in grape seeds

Average oil content in the seed dry matter in the grapevine varieties analysed in 2011 was 11.60 ± 0.33 g/100 g with median 12.37 ± 0.19 g/100 g and oil content ranged from 3.91 ± 0.04 g/100 g in the Zenit variety to 17.32 ± 0.11 g/100 g in the Chardonnay variety (Fig. 1). High oil content was found in the Muscat Dessertnyi (15.94 ± 0.67 g/100 g), Zweigeltrebe (15.59 ± 0.14 g/100 g), Aromatic Riesling (15.42 ± 0.29 g/100 g), André (15.42 ± 0.15 g/100 g) and Riesling Weiss (Rheinriesling, 15.23 ± 0.09 g/100 g) varieties. Our results are comparable with recent data published elsewhere. Atolani, Omere, Otuechere, and Adewuyi (2012) determined yield of grape seed oil 9.58 g/100 g in Nigeria. In another study of Turkish grape seeds the values were higher, ranging from 13.1 ± 0.47 g/100 g in Kalecik Karası to 19.6 ± 0.59 g/100 g in Öküzgözü for wine varieties and from 11.6 ± 0.38 g/100 g in Çavuş to 18.1 ± 0.54 g/100 g in the Amasya Beyazı in the table varieties (Baydar & Akkurt, 2001). In the Pinot Noir and Riesling the levels 17.8 ± 0.88 g/100 g and 16.0 ± 0.23 g/100 g were determined, respectively. In the Kalecik Karası oil content was evaluated as 12.35 ± 0.45 g/100 g and in the Hasandede 16.00 ± 0.69 g/100 g (Baydar, Özkan, & Çetin, 2007). Also in Brazil grape seeds total lipids were determined in the range from 10.84 ± 0.12 g/100 g (cv. Isabel) to 13.72 ± 0.14 g/100 g (cv. Benitaka) (Santos et al., 2011). By pure supercritical CO_2 fluid extraction of grape seed oil the maximum yield reached 6.2 g/100 g or 4.0 g/100 g by addition of ethanol as a modifier (Cao & Ito, 2003).

3.2. Content and fatty acids composition in grape seeds

From the harvest in 2011, 41 grape varieties were analysed for the FA acid content in grape seed oils (Tables 1 and 3). Linoleic acid was the most abundant fatty acid in all analysed oils contributing between 68.10 g/100 g and 78.18 g/100 g oil; the highest amounts were contained in the grape varieties Aurora (78.18 g/100 g), Pálava (77.23 g/100 g), Veltliner Green (77.19 g/100 g), Záhoranka (76.90 g/100 g), Muscat Early (76.58 g/100 g) and Auxerrois (76.05 g/100 g). α-Linolenic acid was present only in very low quantities ranging from 0.29 g/100 g to 0.77 g/100 g. The highest amounts were present in the varieties Zenit (0.77 g/100 g), Veltliner Green (0.62 g/

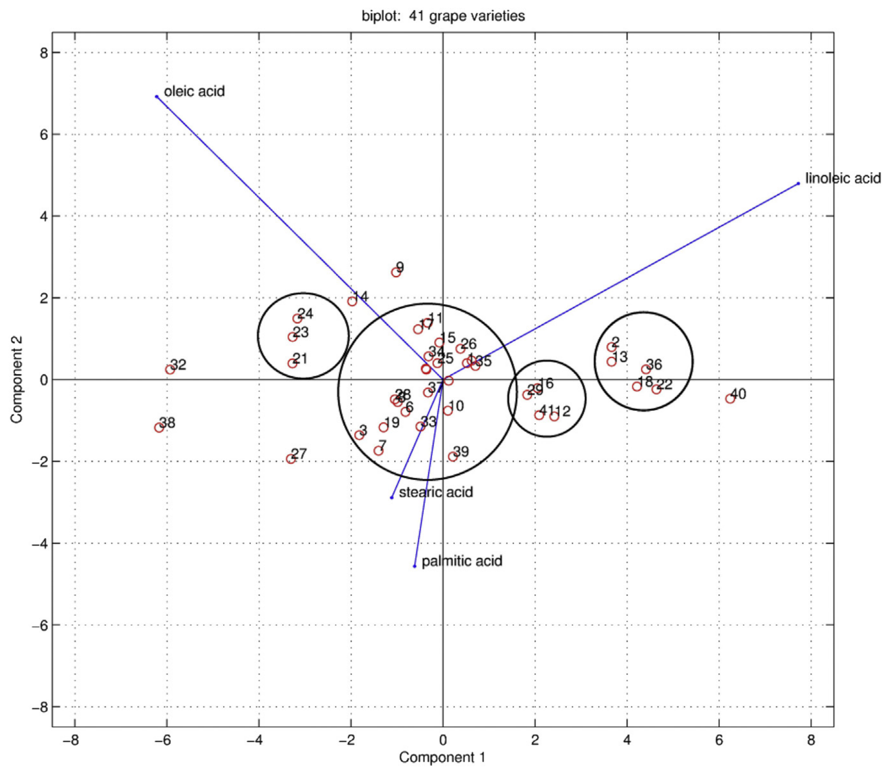

Fig. 2. Principal component analysis of grape varieties and their major FA contents 1-André, 2-Záhoranka, 3- Dornfelder, 4- Aromatic Riesling, 5-Pinot Noir, 6- Silvaner Green, 7-Zenit, 8- Madeleine Angevine, 9-Dětskij Rannij, 10-Bratislava White, 11-Rheinriesling, 12-Siegerrebe, 13- Auxerrois, 14-Muscat Ferdinand Lesseps, 15-Riesling Red, 16- Jacobsteiner, 17-Jaeger, 18-Muscat Early, 19-Pinot Noir Précoce, 20-Muscat Dessertnyi, 21-Děvín, 22-Veltliner Green, 23-Riesling Italian, 24-Pinot Blanc, 25-Zweigeltrebe, 26-Kerner, 27-Muscat Moravian, 28-Blue Portugal, 29-Müller Thurgau, 30-Pinot Noir Swiss selection, 31-Bacchus, 32-Chardonnay, 33-Silvaner Early, 34-Pinot Meunier, 35-Muscat Oberlin, 36-Pálava, 37-Veltliner Red, 38-Mathias János, 39-Basilicum, 40-Aurora, 41-Sauvignon.

100 g), Bratislava White (0.59 g/100 g), Siegerrebe (0.63 g/100 g), Pinot Noir Précoce (0.54 g/100 g), and Aurora (0.52 g/100 g). Oleic acid content ranged between 8.67 g/100 g and 16.78 g/100 g, with the highest content in Chardonnay (16.78 g/100 g), Riesling Italian (16.26 g/100 g), Pinot Blanc (15.88 g/100 g), Mathias János (15.80 g/100 g), Muscat Ferdinand Lesseps (15.41 g/100 g), Dětskij Rannij (15.26 g/100 g) and Děvín (15.11 g/100 g). Thus, oleic acid highly prevailed within MUFA content (Tables 2 and 3), which ranged from 8.82 g/100 g to 16.92 g/100 g with the highest concentrations contained in Chardonnay (16.92 g/100 g), Riesling Italian (16.42 g/100 g), Pinot Blanc (16.05 g/100 g), Mathias János (15.96 g/100 g), Muscat Ferdinand Lesseps (15.52 g/100 g), Dětskij Rannij (15.37 g/100 g) and Děvín (15.24 g/100 g). PUFA content is in agreement with content of linoleic and oleic acids with the highest values found for Aurora (79.01 g/100 g), Veltliner Green (77.95 g/100 g), Pálava (77.78 g/100 g), Záhoranka (77.49 g/100 g), Muscat Early (77.25 g/100 g) and Auxerrois (76.62 g/100 g). These varieties seem to be promising sources of PUFA desirable in human nutrition. High PUFA content may be assigned to high linoleic acid content in Pálava, Záhoranka, Muscat Early and Auxerrois, and in addition, in Veltliner Green to both linoleic and linolenic acids. High content of oleic acid contributed predominantly to high content of MUFA in Chardonnay, Pinot Blanc, Mathias János, Riesling Italian, Ferdinand Lesseps Muscat, Dětskij Rannij and Děvín grape varieties.

SFA ranged between 9.04 g/100 g and 12.82 g/100 g with the highest values in Sauvignon (12.31 g/100 g), Muscat Moravian (12.82 g/100 g), Zenit (12.76 g/100 g), Mathias János (12.59 g/100 g), Silvaner Early (12.54 g/100 g), Chardonnay (12.51 g/100 g) and Sauvignon (12.31 g/100 g). Higher values were determined for the content of palmitic acid (4.93–8.02 g/100 g) as compared to stearic acid (2.91–5.65 g/100 g). Higher levels of palmitic acid were found in the Silvaner Green (8.02 g/100 g), Silvaner Early (8.00 g/100 g), Dornfelder (7.91 g/100 g), Muscat Moravian (7.89 g/100 g), Zenit (7.83 g/100 g) and Bratislava White (7.72 g/100 g), while those of stearic acid in Chardonnay (5.65 g/100 g), Sauvignon (5.51 g/100 g), Děvín (5.24 g/100 g), Madeleine Angevine (4.96 g/100 g), Mathias János (4.74 g/100 g) and Basilicum (4.59 g/100 g).

Content of *trans*-FA was negligible (0.02–0.15 g/100 g) and the lowest concentrations were typical for the Silvaner Green, André, Děvín, Chardonnay, Pinot Meunier, Pálava, Veltliner Green, Pinot Noir Swiss, Pinot Noir, Pinot Blanc, Riesling Red, Rheinriesling, Riesling Italian, Aromatic Riesling and Záhoranka varieties. Higher SFA content was contributed to mainly by palmitic acid in the Silvaner Early, Muscat Moravian and Zenit and stearic acid in Chardonnay, Sauvignon and Mathias János varieties. Statistical evaluation proved evident, very close correlations between PUFA and linoleic acid contents ($R^2 = 0.998$) and between MUFA and oleic acid contents ($R^2 = 0.994$). High correlations were also found between linoleic and oleic acid contents ($R^2 = 0.969$) and SFA and palmitic acid contents ($R^2 = 0.969$). Likewise high relationships between SFA and stearic acid contents ($R^2 = 0.904$), linolenic and oleic acid contents ($R^2 = 0.901$), PUFA and linolenic acid contents ($R^2 = 0.900$) and linoleic and linolenic acid contents ($R^2 = 0.898$) were found.

These results fall within similar ranges reported in the literature (Lutterodt, Slavin, Whent, Turner, & Yu, 2011). In grape oil separated by capillary gas chromatography Řezanka and Řezanková (1999) found dominant FA linoleic acid (67.2 g/100 g) and oleic acid (22.1 g/100 g), and in lesser amounts palmitic acid (7.0 g/100 g) and stearic acid (3.0 g/100 g). Only traces of linolenic (0.5 g/100 g), C:20:0 and C:16:1 acids (0.1 g/100 g) were determined. Seeds presented the largest FA concentrations, as reported by Santos et al. (2011). The main monounsaturated fatty acid (MUFA) in seeds was oleic acid. Besides a high content of linoleic acid, which is a precursor of long-chain fatty acids of the n-6 series, the analysed grapes also contained α-linolenic acid (18:3n-3), a precursor of the n-3 series. The omega-6/omega-3 (n-6/n-3) ratio in seeds of the different varieties was comparable with data of Santos et al. (2011), ranging from 93 to 235 and was relatively high. In relation to this ratio, the varieties with the lowest ratio were Zenit, Bratislava White, Siegerrebe, Pinot Noir Early, Děvín and Aurora. The lower n-6/n-3 ratio in these varieties provides a better choice from this point of nutrition (Wijendran & Hayes, 2004). When considering the general classification of the fatty acids, it was found that the grape seed oils had the following order: PUFA > MUFA > SFA, which is in agreement with other studies (Fernandes, Casal, Cruz, Pereira, & Ramalhosa, 2013; Pardo, Fernández, Rubio, Alvaruiz, & Alonso, 2009; Tangolar et al., 2009). In grape seed oils of 10 Portuguese varieties the lipid fraction was also composed mainly by linoleic acid, followed by oleic acid, palmitic acid and stearic acid as major components of grape seed oil. In addition to these main fatty acids we also identified α-linolenic acid in low quantities. However, low levels of linolenic acid may be desired in edible oils, while high levels of this fatty acid can produce oxidised unfavourable products due to having three double bonds. So, grape seed oil possessing low amounts of linolenic acid can be an advantage in terms of human consumption and the shelf-life of the oil (Baydar et al., 2007). Only a negligible contribution has been found for other fatty acids such as myristic, arachidic, behenic, palmitoleic, eicosenoic, eicosadienoic acids and others presented in negligible amounts (their portion was evaluated as 0.65–2.79 g/100 g). Similar results were found in Turkish grape seed oils, where in some varieties eicosenoic acid content was similar to linolenic acid (Aydin & Ozcan, 2012; Baydar & Akkurt, 2001; Canbay & Bardakçi, 2011).

Principal component analysis (Fig. 2) revealed three groups, where within the group similar grape varieties could be identified. The first group was represented by the Záhoranka, Auxerrois, Muscat Early, Pálava and Veltliner Green varieties, in the second group the Siegerrebe, Jacobsteiner, Müller Thurgau and Sauvignon and in the third group the Děvín, Riesling Italian and Pinot Blanc varieties were included. Completely different from other varieties and each other were the Dětskij Rannij, Muscat Ferdinand Lesseps, Muscat Moravian, Chardonnay, Mathias János and Aurora varieties. Among other varieties no significant differences were found and could be included in the same group.

In the years 2011 and 2012 the average temperatures were equal with the value 9.6 °C, however a difference in the sum of precipitation was observed – 745.7 and 596.2 mm in 2011 and 2012, respectively. Accordingly, the year 2012 in comparison with 2011 was drier. An average decrease of stearic acid, linoleic acid, linolenic acid, SFA, and PUFA has been determined in the year 2012, whereas palmitic and oleic acid showed an increase of the values in 2012 (Tables 1 and 2).

4. Conclusion

Linoleic acid was the most abundant fatty acid in all analysed grape seed oils, contributing between 68.10 g/100 g and 78.18 g/100 g oil. The highest amounts were contained in the grapevine varieties Aurora, Pálava, Veltliner Green, Záhoranka and Muscat Early. Linolenic acid was present only in a low proportion ranging from 0.29 g/100 g to 0.77 g/100 g. Oleic acid content conformed to MUFA content, which ranged from 8.82 g/100 g to 16.92 g/100 g with the highest concentrations contained in Chardonnay, Pinot Blanc and Riesling Italian. High PUFA content may be assigned to high linoleic acid content. SFA ranged between 9.04 g/100 g and 12.82 g/100 g and higher values were determined for the content of palmitic acid as compared to stearic acid. Statistical evaluation proved evident, very close correlation between PUFA and linoleic acid ($R^2 = 0.998$) and between MUFA and oleic acid content ($R^2 = 0.994$). It was found that the grape seed oils had the following order: PUFA > MUFA > SFA. Principal component analysis of the content of major fatty acids revealed three different groups of varieties; some other varieties differed significantly each other, and all other remaining varieties did not differ significantly. The year of harvest showed different effect on the content of individual FA.

Acknowledgements

This work was supported by a grant project *NAZV QI111B107* of the Ministry of Agriculture of the Czech Republic and a project of the Ministry of Education, Science, Research and Sport of the Slovak Republic and EU Building Research Centre AgroBioTech No. 26220220180.

References

Atolani, O., Omere, J., Otuechere, C. A., & Adewuyi, A. (2012). Antioxidant and cytotoxicity effects of seed oils from edible fruits. *Journal of Acute Disease*, 130–134.

Aydin, A., & Ozcan, B. C. (2012). *Fatty acid compositions of seeds of some grape cultivar (Vitis vinifera L.) grown in Turkey*. Athens, Atinerś Conference Paper Series, No. AGR2012-0226.

Bail, S., Stuebiger, G., Krist, S., Unterweger, H., & Buchbauer, G. (2008). Characterization of various grape seed oils by volatile compounds, triacylglycerol composition, total phenols and antioxidant capacity. *Food Chemistry, 108*, 1122–1132.

Baydar, N. G., & Akkurt, M. (2001). Oil content and oil quality properties of some grape seeds. *Turkish Journal of Agriculture and Forestry, 25*, 163–168.

Baydar, N. G., Özkan, G., & Çetin, E. S. (2007). Characterization of grape seed and pomace oil extracts. *Grasas y Aceites, 58*, 29–33.

Bellido, C., López-Miranda, J., Pérez-Martínez, P., Paz, E., Marín, C., Gómez, P., et al. (2006). The Mediterranean and CHO diets decrease VCAM-1 and E-selectin expression induce by low density lipoprotein in HUVECs. *Nutrition, Metabolism, and Cardiovascular Diseases, 16*, 524–530.

Beveridge, T. H. J., Girard, B., Kopp, T., & Drover, J. C. G. (2005). Yields and composition of grape seed oils extracted by supercritical carbon dioxide and petroleum ether: Varietal effects. *Journal of Agricultural and Food Chemistry, 53*, 1799–1804.

Canbay, H. S., & Bardakçi, B. (2011). Determination of fatty acid, C, H, N and trace element composition in grape seed by GC/MS, FTIR, elemental analyzer and ICP/OES. *SDU Journal of Science, 6*, 140–148.

Cao, X., & Ito, Y. (2003). Supercritical fluid extraction of grape seed oil and subsequent separation of free fatty acids by high-speed counter-current chromatography. *Journal of Chromatography A, 1021*, 117–124.

Crews, C., Hough, P., Godward, J., Brereton, P., Lees, M., Guiet, S., et al. (2006). Quantitation of the main constituents of some authentic grape-seed oils of different origin. *Journal of Agricultural and Food Chemistry, 54*, 6261–6265.

Fernandes, L., Casal, S., Cruz, R., Pereira, J. A., & Ramalhosa, E. (2013). Seed oils of ten traditional Portuguese grape varieties with interesting chemical and antioxidant properties. *Food Research International, 50*, 161–166.

Gebauer, S., Harris, W. S., Kris-Etherton, P. M., & Etherton, T. D. (2005). Dietary n-6: n-3 fatty acid ratio and health. In C. C. Akoh, & O.-M. Lai (Eds.), *Healthful lipids* (pp. 221–248). Champaign: AOCS Press.

Hanganu, A., Todaşcă, M.-C., Chira, N.-A., Maganu, M., & Roşca, S. (2012). The compositional characterisation of Romanian grape seed oils using spectroscopic methods. *Food Chemistry, 134*, 2453–2458.

Lutterodt, H., Slavin, M., Whent, M., Turner, E., & Yu, L. (2011). Fatty acid composition, oxidative stability, antioxidant and antiproliferative properties of selected cold-pressed grape seed oils and flours. *Food Chemistry, 128*, 391–399.

Pardo, J. E., Fernández, E., Rubio, M., Alvaruiz, A., & Alonso, G. I. (2009). Characterization of grape seed oil from different grape varieties (*Vitis vinifera*). *European Journal of Lipid Science and Technology, 111*, 188–193.

Řezanka, T., & Řezanková, H. (1999). Characterization of fatty acids and triacylglycerols in vegetable oils by gas chromatography and statistical analysis. *Analytica Chimica Acta, 398*, 253–261.

Santos, L. P., Morais, D. R., Souza, N. E., Cottica, S. M., Boroski, M., & Visentainer, J. V. (2011). Phenolic compounds and fatty acids in different parts of *Vitis labrusca* and *V. vinifera* grapes. *Food Research International, 44*, 1414–1418.

Simionato, J. I., Garcia, J. C., dos Santos, G. T., Oliveira, C. C., Visentainer, J. V., & de Souza, N. E. (2010). Validation of the determination of fatty acids in milk by gas chromatography. *Journal of the Brazilian Chemical Society, 21*, 520–524.

Tangolar, S. G., Ozoğul, Y., Tangolar, S., & Torun, A. (2009). Evaluation of fatty acid profiles and mineral content of grape seed oil of some grape. *International Journal of Food Sciences and Nutrition, 60*, 32–39.

Wijendran, V., & Hayes, K. C. (2004). Dietary n-6 and n-3 fatty acid balance and cardiovascular health. *Annual Review of Nutrition, 24*, 597–615.

Yi, C., Shi, J., Kramer, J., Xue, S., Jiang, Y., & Zhang, M. (2009). Fatty acid composition and phenolic antioxidants of winemaking pomace powder. *Food Chemistry, 114*, 570–576.