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Fatty Acid Composition, Tocopherols and β-Carotene Content in Polish Commercial Vegetable Oils

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Abstract: The fatty acid composition, tocopherols and β-carotene content in the following vegetable oils: rapeseed, olive, arachide, sunflower, soybean, corn, grapeseed, pumpkin seed, sesame and linseed were evaluated. The study comprised commercial refined and cold pressed oils from different manufacturers. The fatty acid composition was determined by Gas Chromatography (GC) method on a 50m capillary column with a CP Sil 88 phase. α-, β-, γ-, δ-tocopherols and β-carotene contents were analyzed by HPLC method with a Lichrospher Si 60 column. The study showed that β-carotene was present only in some cold pressed oils. The amount of tocopherols varied much between oil types and between the same type of oil from different producers. Among all tested oils, sunflower oil had the highest vitamin E content. The rapeseed oil, the most popular on Polish market was characterized by the highest content of α-linolenic acid and the lowest 18:2/18:3 ratio. The α-tocopherol equivalent to polyenoic content ratio was the highest in olive oil and the lowest in commercial linseed oil. Only 1.6% of linolenic acid in the total fatty acid composition was observed in the linseed oil.

Key words: Vegetable oils, fatty acids, tocopherols, β-carotene

Introduction

In recent years, a high part of vegetable oils in Polish diet has been observed. The vegetable oils are dietary sources of unsaturated fatty acids and vitamin E. The fatty acid composition and an unsaponifiable substances content in oilseeds depend on the plant species, degree of ripening seeds and the climatic conditions. The composition of unsaponifiable lipids in oils is influenced also by processing and storage condition of oil. The losses of tocopherols during storage of oils depend on the kind of oil, storage temperature, kind of packaging and access of light and oxygen (Nogala-Kałucka, 2003).

There are a lot of different oils on Polish market. Mostly, they are refined, but there are also cold pressed oils. The composition of fatty acids is often the only information provided in studies on vegetable oils (Daniewski *et al*., 2000; (Daniewski *et al*., 2003; Gajewska *et al*., 1996; Przysławski *et al*., 1996). Data on vitamin content in vegetable oils are limited (Okolska *et al*., 1988; Mińkowski, 2001). Hence, the aim of this study was to determine the fatty acid composition, tocopherols and β-carotene content in refined and cold pressed commercial vegetable oils.

Materials and Methods

The oils were purchased from the local retail stores in Olsztyn (Poland). The study comprised refined oils: 8 (different producers) rapeseed oils, 2 arachide oils, 3 sunflower oils, 2 soybean oils and olive and corn oil. Also 10 cold pressed oils: rapeseed, olive, arachide, sunflower, soybean, corn, grapeseed, pumkin seed, sesame and linseed with decreased linolenic acid content were analyzed. The oils were produced by different manufacturers. Some oils were produced in Poland and others were imported. All oils were purchased and analyzed within the recommended period of consumption.

Determination of fatty acid composition: The fatty acid composition was determined by Gas Chromatography (GC) on a Hewllett-Packard 6890 chromatograph (Palo Alto, CA) equipped with split/split less injection port and a flame ionization detector. Fatty Acid Methyl Esters (FAMEs) of the oils were prepared by Peisker's method as modified by Żegarska *et al*. (1991). FAMEs were separated using a CP Sil 88 (0.20 μm) capillary column 50 m long and 0.25 mm diameter. The column temperature was 180°C. Injector and detector temperatures were both 250°C. Helium carrier gas flow was 1.0 ml/min at a split ratio 1:50. The results are given in weight percentage.

Determination of β-carotene and tocopherols content: Contents of β-carotene and tocopherols were determined by HPLC method. Analyses were performed based on the method by Chase *et al*. (1994).

Sample preparation for HPLC. About 1g of oil was weighed into 10 mL measuring flask with the 0.0001g accuracy. The content of flask was completed with hexane, mixed until the oil was dissolved, left for 12 h in dark and then centrifuged at 500 rpm in a laboratory centrifuge.

Table 1: Fatty acid composition of refined and cold pressed oils (percentage of total fatty acids)

Oils		16:0	18:0	20:0	22:0	16:1	18:1 c9	18:1 c11	20:1	22:1	18:2	18:3	Others*	18:2/ 18:3 ratio
		Saturated				Monoenoic					Polyenoic			
		---------- Fatty acids ---------												
		---------- Refined Oils ---------												
Rapeseed	1	4,7	1,8	0,6	0,3	0,2	58,1	4,7	1,3	0,9	17,0	8,0	2,4	2,1
	2	4,6	1,6	0,6	0,3	0,2	55,4	4,9	1,4	1,3	18,3	9,3	2,1	2,0
	3	4,6	1,8	0,6	0,3	0,2	61,0	2,3	1,3	0,8	17,0	8,1	2,0	2,1
	4	4,8	1,7	0,6	0,3	0,2	56,3	5,9	1,3	0,9	17,1	8,6	2,3	2,0
	5	5,5	1,9	0,6	0,3	0,2	52,0	6,4	1,6	1,5	20,4	7,0	2,6	2,9
	6	4,7	1,7	0,6	0,3	0,2	56,8	5,8	1,3	0,8	17,0	8,2	2,6	2,1
	7	4,8	1,8	0,6	0,3	0,1	57,8	5,9	1,2	0,6	16,2	7,9	2,8	2,0
	8	5,1	1,8	0,6	0,2	0,2	55,8	6,8	1,3	0,8	17,0	8,2	2,2	2,1
Arachide	1	10,5	3,5	1,5	2,5	0,3	55,7	2,6	0,9	0,1	18,5	0,3	3,6	61,7
	2	11,4	3,7	1,6	2,6	0,2	53,2	2,3	0,9	0,1	19,9	0,2	3,9	99,5
Sunflower	1	7,3	3,8	0,3	0,6	0,1	24,3	2,5	0,2	0,0	57,7	0,4	2,8	144.2
	2	6,9	4,0	0,4	0,7	0,1	28,5	3,0	0,2	0,0	52,8	0,4	3,0	132,0
	3	6,9	3,5	0,4	0,6	0,1	27,0	2,6	0,1	0,0	55,5	0,2	3,1	277,5
Soybean	1	10,6	3,3	0,5	0,5	0,2	27,4	3,0	0,4	0,3	46,0	5,8	2,0	7,9
	2	11,0	3,3	0,4	0,4	0,2	27,0	3,6	0,3	0,2	46,0	5,4	2,2	8,5
Olive	1	11,8	2,9	0,5	0,2	0,7	65,9	3,3	0,3	0,0	10,5	0,7	3,2	15,0
Corn	1	12,9	2,1	0,6	0,2	0,2	28,5	2,4	0,2	0,0	49,3	0,8	2,8	61,6
		---------- cold pressed oils ---------												
Rapeseed		4,9	1,9	0,7	0,4	0,2	58,5	3,6	1,2	0,5	17,0	7,4	3,6	2,3
Olive		11,3	3,0	0,4	0,1	0,8	72,3	2,4	0,2	0,0	5,8	0,7	3,5	8,3
Arachide		11,4	4,3	1,8	3,0	0,2	36,3	1,9	0,8	0,0	36,5	0,2	3,7	182,5
Sunflower		7,5	3,9	0,5	0,7	0,1	17,6	2,1	0,2	0,0	62,9	2,1	2,4	30,0
Soybean		11,3	3,2	0,5	0,3	0,2	25,0	2,4	0,2	0,0	52,4	2,3	2,9	22,8
Corn		12,0	1,8	0,5	0,1	0,2	26,1	2,3	0,2	0,0	53,6	0,8	2,6	67,0
Grapeseed		7,6	4.1	0,3	0,1	0,1	14,5	1,8	0,2	0,0	68,2	0,4	2,6	170,5
Pumpkin seed		11,9	6,4	0,5	0,1	0,2	36,8	2,3	0,1	0,0	39,2	0,3	2,1	130,7
Sesame		10,0	5,2	0,7	0,2	0,2	35,8	2,4	0,2	0,0	42,4	0,7	2,8	60,6
Linseed		7,0	3,7	0,3	0,2	0,1	15,0	1,8	0,1	0,0	67,4	1,6	2,6	42,1

* - 14:0, 14:1, 15:0, 15:1, 24:0 and unidentified fatty acids

HPLC separation. HPLC analysis was performed using a HP 1050 chromatograph (Hewlett Packard, Waldbronn, Germany) with a spectrometric detector UV-VIS model HP1050 combined with a fluorescence detector model HP 1046A. Injector volume: 50 µL. Column: 250 mm×4 mm with Lichrospher Si 60 (5 µm). Mobile phase: hexane/2-propanol 99.3:0.7, flow: 1ml/min. Detection: β-carotene - UV - VIS detector, λ = 450nm; tocopherols-fluorescence detector, λ_{ex} = 295nm, λ_{em} = 330nm. The peaks were identified by comparing the retention times for the samples of oil and standard solutions of known concentration of β-carotene and four tocopherols. The standard solutions of β-carotene and α, β, γ and δ-tocopherols were prepared from Merck (Darmstadt, Germany) vitamin standards. The content of the examined compounds expressed in mg/100 g oil was computed by comparing the area of peaks after chromatographic separation of standard solutions and examined samples.

All samples of oils were prepared in duplicate and determination for each sample were done twice.

Results and Discussion

The results of determination of fatty acid composition (Table 1) indicate that both rapeseed and olive oils have a high content of oleic acid. The level of this acid in the olive oil was ca. 70% of total fatty acids. From nutritional viewpoint, the presence of oleic acid in diet is very useful. It has been shown that oleic acid is effective in lowering LDL content and LDL cholesterol content (Grundy, 1989). Compared with the olive oil, the rapeseed oil has ca. 10 percentage units less of oleic acid, also ca. 2 times less of saturated acids and more polyenoic acids (Table 1). The content of erucic acid in the tested rapeseed oils was in the range of 0.5 to 1.5%. The high level of oleic acid was also found in refined arachide oil. Compared with the rapeseed oils, the refined arachide oils (Table 1) have similar level of oleic and linoleic acid, less linolenic acid and more saturated acids. The cold pressed arachide oil had similar quantity of oleic and linoleic acids. Such considerable differences in fatty acid composition of arachide oils may be caused by the region in which the peanuts are grown.

Table 2: Tocopherol and β-carotene content of refined and cold pressed oils (mg/100g)

Oils		Tocopherol α	β	γ	δ	α-$T_{eq.}$[a]	α-T_{eq}/∑ PEFA[b]
				--------- Refined Oils* ---------			
Rapeseed	1	33,60	-	43,32	-	37,93	1,52
	2	28,15	-	37,16	-	31,87	1,15
	3	36,20	-	53,58	0,50	41,56	1,66
	4	35,63	-	38,12	-	39,44	1,53
	5	28,04	-	37,01	-	31,74	1,16
	6	32,32	-	47,80	0,32	37,10	1,47
	7	30,81	-	39,43	-	34,75	1,44
	8	29,62	-	43,83	0,48	34,01	1,35
Arachide	1	16,33	-	10,49	-	17,38	0,92
	2	14,30		10,62	-	15,36	0,76
Sunflower	1	62,02	1,85	1,65	-	62,93	1,08
	2	74,80	-	3,06	-	75,11	1,41
	3	64,09	-	-	-	64,09	1,15
Soybean	1	27,90	-	38,77	15,50	31,92	0,62
	2	28,23	1,87	46,60	13,03	33,77	0,66
Olive	1	29,29	-	-	-	29,29	2,62
Corn	1	26,15	-	44,31	-	30,58	0,61
				--------- Cold pressed oils ---------			
Oils	β-carotene	Tocopherol α	β	γ	δ	α-$T^{a}_{eq.}$	α-T_{eq}/Σ_PEFA[b]
Rapeseed	8,09	15,90	-	28,16	0,81	18,72	0,77
Olive	2,61	20,78	-	1,80	-	20,96	3,22
Arachide	0,37	21,30	0,82	32,01	9,46	24,92	0,68
Sunflower	-	60,68	-	-	-	60,68	0,93
Soybean	2,73	24,16		33,17	14,93	27,63	0,51
Corn	3,56	27,22	-	91,76	5,93	36,46	0,67
Grapeseed	-	19,32	-	-	-	19,32	0,28
Pumpkin seed	15,01	10,37	-	48,57	4,90	15,28	0,39
Sesame	-	-	-	50,32	-	5,03	0,12
Linseed	15,01	-	-	29,84	-	2,98	0,04

* - β-carotene was absent in refined oils; a -α-tocopherol equivalent; b- α-tocopherol equivalent to polyenoic fatty acids ratio

The peanut oils from South America have a similar content of C18:1 and C18:2 acids, but the peanut oils produced in Africa have two times more C18:1 acid than C18:2 acid (Belitz and Grosch, 1987).

The sesame and pumpkin seed oils are characterized by similar fatty acid composition. The level of oleic acid in these oils was ca. 36 and 37% and linoleic acid ca. 42 and 39%, respectively. The content of linolenic acid in sesame and pumpkin seed oils was very low, 0.7 and 0.3% of the total fatty acids. The linseed oil contained only 1,6% of linolenic acid.

The sunflower, soybean and corn oils contain high amounts of linoleic acid, but the highest level of this acid (ca. 68% of total fatty acids) was found in linseed and grapseed oils.

Among all tested oils, the highest content of linolenic acid was in rapeseed oil. The samples of rapeseed oils from different producers contained linolenic acid in the amounts of 7 to 9.3%. Hence, rapeseed oil has beneficial proportion of polyenoic fatty acids and improves the n-6/n-3 ratio in diet. The ratio of linoleic to α-linolenic acid in the diet should be between 5:1 and 10:1 (FAO Food and Nutrition paper, 1994). Excessive amounts of n-6 polyenoic acid and very high n-6/n-3 ratio promote the pathogenesis of many diseases, including cardiovascular disease, cancer and inflammatory and autoimmune diseases (Simopoulos, 2002).

The results of this study show that β-carotene was present only in cold pressed oils. The high content of β-carotene was in pumpkin seed and linseed oils (about 15mg/100g) (Table 2). The presence of β-carotene in edible oils is very important because it is effective natural antioxidant. β-carotene has a potential to act as a lipid-soluble chain-breaking antioxidant at low partial pressures of oxygen found in mammalian tissues. It complements the role of vitamin E, which is effective at high oxygen pressures (Burton, 1989). However, β-carotene was absent in some cold pressed oils: sunflower, grapeseed and sesame. We do not know the history of storage conditions of these commercial oils. β-

carotene in raw materials is sensitive to light, the storage temperature and atmosphere (Nogala-Kałucka, 2003).

Both refined and cold pressed oils showed a wide range in tocopherols content. α-tocopherol was present in all tested oils, with the exception of sesame and linseed oil (Table 2). The highest amounts of α-tocopherol were both in refined and cold pressed sunflower oils. The high content of α-tocopherol in sunflower oil is with agreement with data of Kamel-Eldin and Andersson (1997). Their results showed a positive correlation (r = 0.549) between linoleic acid and α-tocopherol in vegetable oils.

The high level of γ-tocopherol was found in soybean, corn, sesame and also rapeseed oils. The rapeseed oils contained γ-tocopherol in the range of 28.16 to 53.58 mg/100 g. The results obtained are almost in agreement with the data of Koski *et al.* (2002). They found that γ-tocopherol in rapeseed oil was in the range of 524 to 632 ppm. The study of Kamel-Eldin and Andersson (1997) suggested a positive correlation between linolenic acid and γ-tocopherol.

β-and δ-tocopherols were observed only in some of the tested oils. The highest δ-tocopherol level was in the soybean oils (13.03-15,50 mg/100g).

α-tocopherol is characterized by a full biological activity. The biological activity of remaining forms is much lesser. β-tocopherol possesses 40%, γ-tocopherol-10% and δ-tocopherol only 1% of biological activity of α-tocopherol (Nogala-Kałucka, 2003). Calculated on this basis the α-tocopherol equivalents (Table 2) indicate that the highest content of vitamin E was in sunflower oil. The lowest content of vitamin E was in the linseed oil with a decreased quantity of linolenic acid and sesame oil. Taking into consideration the ratio α-tocopherol equivalent to polyenoic fatty acids content, it is seen that olive oil has the highest values compared to other tested oils. These values for olive oils are in agreement with those reported by Andrikopoulos *et al.* (1989).

In summary, the results of this study show that from the nutritional viewpoint, rapeseed oil, besides olive oil, appears to have a beneficial effect on health. Among the tested oils, rapeseed oil has the highest level of α-linolenic acid, which is usually in insufficient amounts in diet and the lowest ratio of linoleic acid to α-linolenic acid. Tocopherol levels (γ- and α-tocopherols) in this oil appear to be adequate to stabilize its unsaturated fatty acids.

References

Andrikopoulos, N.K., M.N. Hassapidou and A.G. Manoukas, 1989. The tocopherol content of Greek olive oils. J. Sci. Food Agric., 46: 503-509.

Belitz, D. and W. Grosch, 1987. Food chemistry. Springer-Werlag, Berlin, pp: 472-482.

Burton, G.W., 1989. Antioxidant action of carotenoids. J. Nutr., 119: 109-111.

Chase, W.G., C.C. Akoh and R.R. Eitenmiller, 1994. Analysis of tocopherols in vegetable oils by high-performance liquid chromatography: comparison of fluorescence and evaporative light-scattering detection. J. Am. Oil Chem. Soc., 71: 877-880.

Daniewski, M., E. Mielniczuk, B. Jacórzyński, J. Balas, M. Pawlicka, A. Filipek and M. Górnicka, 2000. Charakterystyka składu kwasów tłuszczowych wybranych olejów roślinnych. (Fatty acid contents of selected plant oils). Bromat. Chem. Toksykol., XXXIII: 215-219.

Daniewski, M., B. Jacórzyński, A. Filipek, J. Balas, M. Pawlicka and E. Mielniczuk, 2003. Skład kwasów tłuszczowych wybranych olejów jadalnych. (Fatty acid content in selected edible oils). Roczn. PZH, 54: 263-267.

FAO Food and Nutrition Paper, 1994. Fats and oils in human nutrition: report of a join expert consultation. No 57.

Gajewska, R., E. Ledóchowska and Z. Ganowiak, 1996. Ocena stopnia świeżości oraz skład kwasów tłuszczowych olejów jadalnych i margaryny niskokalorycznej. (Freshness evaluation and fatty acid content of edible oils and low calorie margarine-mini light). Bromat. Chem. Toksykol., XXIX: 329-333.

Grundy, S.M., 1989. Monounsaturated fatty acids and cholesterol metabolism. Implication for dietary recomendations. J. Nutr., 119: 529-533.

Kamel-Eldin and R. Andersson, 1997. A multivariate study of the correlation between tocopherol content and fatty acid composition in vegetable oils. J. Am. Oil Chem. Soc., 74: 375-380.

Koski, A., E. Psomiadou, M. Tsimidou, A. Hopia, P. Kefalas, K. Wahala and M. Heinonen, 2002. Oxidative stability and minor constituents of virgin olive oil and cold-pressed rapeseed oil. Eu. Food Res. Technol., 214: 294-298.

Mińkowski, K., 2001. Ocena zawartości tokoferoli naturalnych i dodanych w wybranych olejach i margarynach. XXXII Sesja Nauk. KTiChŻ PAN "Technologia żywności a oczekiwania konsumentów" SGGW, Warszawa 6-7 wrzesień 2001.

Nogala-Kałucka, M., 2003. Fat-soluble vitamins. In: Chemical and functional properties of food lipids. Boca Raton. CRC Press, pp: 109-132.

Okolska, G., M. Jelińska, H. Kunachowicz and Ś. Ziemlański, 1988. Zawartośæ kwasów tłuszczowych i witamin A i E w tłuszczach jadalnych. (Fatty acids and vitamins A and E in edible fats). Żyw. Człow. Metabol., XV: 179-188.

Przysławski, J., H. Gertig and J. Nowak, 1996. Analiza składu kwasów tłuszczowych wybranych olejów roślinnych. (Fatty acids content in some vegetable oils). Brom. Chem. Toksykol., XXIX: 335-342.

Simopoulos, A.P., 2002. The importance of the ratio of omega-6/omega-3 essential fatty acids. Biomed Pharmacother, 56: 365-379.

Żegarska, Z., J. Jaworski and Z. Borejszo, 1991. Ocena zmodyfikowanej metody Peiskera otrzymywania estrów metylowych kwasów tłuszczowych. (Evaluation of the modified Peisker method to obtain fatty acid methyl esters). Acta Acad. Agric. Technol. Olst. (Technologia Alimentorum), 24: 25-33.