Chemical composition and stability of rapeseed oil produced from various cultivars grown in Lithuania

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Abstract

The aim of this work was to determine the chemical composition and stability of rapeseed oil produced from 15 various cultivars grown in Lithuania. The chemical composition is the capital point that specifies the quality of rapeseed oil. The quality of rapeseed oil is very important in all the European Union, because rapeseed oil is produced not only as an edible oil but also is of great use in biodiesel production. In the light of these facts, the high quality of the edible rapeseed oil is a matter of great concern. It was proved that oleic fatty acid is the main component of rapeseed oil (65.39%). Furthermore, the ratio of linoleic and of α-linolenic fatty acid was approximately 2:1. Consequently, the oxidative stability and the total amount of phenolic compounds were determined as well. The oxidative stability at 110 °C temperature under 5 bar pressure ranges from 3.71h to 12.71h. The high oxidative stability might be mainly influenced of high amounts of MUFA, low amounts of PUFA and total phenolic compounds. The correlation coefficents between oleic fatty acid and oxidative stability was 0.76, between total phenolic compounds and oxidative stability it was 0.94.

Keywords: rapeseed oil; chemical composition; fatty acids; oxidative stability.

Introduction

The European Union (EU) is encouraging the use of biofuel accordingly to reduce greenhouse gas emission. The EU Biofuels Directive (2003) requires 2 percent of energy for transport to come from renewable sources, including both biodiesel and bioethanol, to be rised to 5.75 percent by the end of 2010, and 20 percent by the year of 2020. Consequently, biodiesel production in EU is well developed. To succeed in project, tremendous amounts of rapeseed harvest are grown in EU [1]. Rapeseed is the most common oil stock used for producing biodiesel in Europe, partly because rapeseed produces more oil per unit of land area as compared to other oil sources [2].

It is evident that rapeseed oil can be used either as food, animal feed or for making biofuels. This is the significant issue on a global scale. Thereby, it is possible that the quality of rapeseed oil, as an edible oil, could be declined, because the rapeseed oil quality for biodiesel production is not so important. Thus, farmers can switch from producing food crops to producing biofuel crops to make more money, even if new kinds are not edible. Conversely, the edible oil is considered to be high quality [3, 4, 5].

On the other hand, rapeseed oil is supposed to be more technical than edible oil. Consumers assume that rapeseed oil is noxious, because they are still not enough informed that the oil which is produced recently differ from the one produced formerly. Aforetime there was only wild type rapeseed oil. It contained 43% of erucic acid. Which is notorious for being harmful for humans [5, 6]. It should be observed that erucic fatty acid can be valuable component of bio-diesel because of high calorific value, low flash point, high octane number and good lubrication characteristics [7, 8].

In consequence of plant breeders efforts, rapeseed oil frequently has less than 2% of erucic fatty acid [6]. Anti-nutritional components such as glucosinolates are reduced either. Hence, the safety of rapeseed oil and meal for human and animal consumption was assured. These breeds of rapeseed are called double zero, with low content of erucic acid and glucosinolates. Today these indexes are still main criterions that evaluates the quality of rapeseed oil. Besides the high-quality oil, the meal from oilseed rape after oil extraction also provides a protein-rich animal feed [9, 10].

Currently, there are new yellow-seeded („000“) strains of rapeseed which are the pride of plant breeders. Lithuanias plant breeders from Lithuanian University of Agriculture are intensely working on investigations and perfection of yellow-seeded strains. They have already reduced glucosinolates and the amount of erucic acid and instead of it increased the oleic fatty acid. These seeds are very high quality because they accumulate more oil, proteins, amino acids and has less of glucosinolates and fibres. Besides, the yellow

seeds have thiner seed-coat than black and less of cellulose and tannins. Such seeds are perfect for edible rapeseed oil production. It is discovered that there are no modeling rapeseed genotypes for yellow-seeded kinds. Wherefore Lithuanias breeders have developed yellow-seeded strains by interspecific cross combinations in a manner of selection [11]. Consequently, the rapeseed oil produced from various cultivars grown in Lithuania does not contain GMO.

The edible rapeseed oil is obtained from low erucic and low glucosinolate *Brassica campestris*, *Brassica napus* and *Brassica juncea* species. It is one of the most important vegetable oil which is used for salad oil, dressings, mayonnaise and margarine as well, because of high oxidative stability [3, 9, 12].

Rapeseed oil is considered by researchers by its unique chemical properties and possibility of the oil to be used in the diet. The excellent nutritional properties of rapeseed oil are based on fatty acid (FA) composition, with a high amount of monounsaturated oleic fatty acid (MUFA) (nearly 60%). Which is the main component (80%) in valuable olive oil and the staple dietary FA [13].

Furthermore, rapeseed oil has a well-balanced ratio between the most important polyunsaturated fatty acids families (PUFA) n-3 and n-6. These compounds are said to be essential because the human body is unable to synthesize them, although it can metabolize them to longer-chain derivatives. So, the diet must cover the organism need for these FA [9, 13, 14].

PUFA is not only presented at conversion into long-chain FA but it is also required for the synthesis of eicosanoids, i.e. leukotrienes and prostaglandins. These are autocrine or paracrine chemical signals acting as cell messengers. This has been an essential issue for nutritionists because these two signal families have antagonistic actions. While n-3 FA give birth to anti-inflammatory, anti-thrombotic, anti-hypertensive and anti-arrhythmic derivatives, n-6 FA generate inflammatory, thrombotic, hypertensive and arrhythmic metabolities [14, 15].

Materials and methods

Materials

There were used only analytic purity methanol and n-hexane purchased from Readl-de Haëun (Seezle, Germany). The standart Folin-Ciocalteau Phenol reagent and boron trifluoride-methanol complex supplied from Merck (Darmstadt, Germany). Sodium carbonate and sodium hydroxide were from Fluka (Buchs, Switzerland). The gallic acid (3,4,5-trihydroxybenzoic acid) was from Sigma Co. (Germany).

Rapeseed cultivars were collected by agribusiness company Linas Agro Group AB. There were analysed 15 various cultivars grown in Lithuania in the year 2008. There were: *Sunday, Landmark, Ural, Kasimir, Heros, Casino, Pastel, Terra, Hendrix, Holiday, Nex180, Paladium, Prima, Senator, Rodeo.*

For 4 hours 25 grams of grained seed were extracted with hexane in Soxhlet extractor at 40-60 ^{0}C. The solvent was evaporated with vacuum rotary evaporator. The oil samples were saturated with nitrogen gas and stored at 4 ^{0}C until analysis.

Methods

The content of the fatty acids (FA) was determined by GC. The oxidative stability (IP) was determined at 110 ºC temperature under 5 bars (500kPa) of oxygene pressure by instrumental Oxipress method [16].

The phenolic compounds were extracted from the oil using modified V.Roncer method. An aliquot (5g) of oil was dissolved in hexane (5ml) and extracted into aqueous 60% methanol (3x6 ml) using a separation funnel. The aqueous fractions were combined, washed with hexane (5ml), filtered and evaporated under vacuum at ~40 ^{0}C. Than the residual sample was evaporated to dryness under nitrogen and 0.1 % methanolic solution was prepared. It was stored at -18 ^{0}C in the dark. The determination of total phenolic compounds (TPC) was accomplished by Folin–Ciocalteu method.

Results and discussion

The content of fatty acids

Data of the study showed that rapeseed oil contains considerable amount (average 65.39%) of oleic fatty acid (MUFA). This demonstrates approximation to prominent olive oil. It was estimated that analysed rapeseed oil moderately contains 18.6% of linoleic and 7.51% of α-linolenic fatty acid (PUFA). As it is seen in table 1, the rapeseed oil cultivars such as *Ural, Nex180 and Holiday* contained the maximum of MUFA (69.12%, 77% and 78.78% respectively) and the minimum of PUFA (23.75%, 17.71% and 15.42% respectively).

Table 1. FA composition (%) of divers cultivars of rapeseed oil

	SFA	C18:1	C22:1	MUFA	C18:2	C18:3	PUFA	n-6/n-3
Sunday	7.07	67.14	0.04	67.46	18.01	7.45	25.47	2.42
Landmark	6.42	63.93	-	64.23	19.70	9.66	29.36	2.04
Ural	7.12	68.21	0.05	69.12	16.72	7.03	23.75	2.38
Kasimir	6.92	62.56	0.05	63.03	19.91	9.09	29.00	2.19
Heros	7.17	62.99	0.06	63.55	20.22	9.06	29.28	2.23
Casino	7.30	62.86	0.06	63.93	19.80	8.18	27.98	2.42
Pastel	6.45	62.91	0.20	64.15	20.85	7.94	28.79	2.63
Terra	6.50	63.57	0.11	64.78	19.14	9.21	28.35	2.08
Hendrix	6.27	62.70	0.14	63.68	19.20	8.31	27.51	2.31
Holiday	5.39	77.66	-	78.78	13.40	2.02	15.42	6.63
Nex180	5.16	75.82	0.18	77.00	15.47	2.24	17.71	6.91
Paladium	6.76	63.48	0.20	64.27	20.95	7.48	28.43	2.80
Prima	6.27	60.62	0.11	61.51	20.60	8.70	29.30	2.37
Senator	5.62	63.29	0.15	64.37	19.61	8.13	27.74	2.41
Rodeo	6.79	65.25	0.13	66.21	18.44	8.33	26.77	2.21

The ratio in table 1 between linoleic and α-linolenic fatty acid (n-6/n-3) is 2:1. This is the exact ratio as it is found in literature [13, 14]. Forasmuch *Holliday* and *Nex180* cultivars had MUFA at most they had PUFA at least. So the ratio for them is an exception (nearly 7:1). Besides, there was estimated that there was no cultivar which had more than 0.2% of erucic acid.

The oxidative stability

It was obtained that the oxidative stabilities at 110 °C temperature of *Nex180* and *Holiday* were incredibly high – IP=12.71h and IP=8.59h (table 2). The facts suggest that these crops which had the biggest amount of MUFA and were low in PUFA were the most stable during the oxidation. Whereas others cultivars IP was 4-7h. The *Nex180* and *Holiday* cultivars belong to yellow-seeded rapeseed. In point of fact, the olein fatty acid is the main cause of improved oxidative stability [17]. Moreover, in this study it was detected that such seeds yield 44±0.04% and 48±0.03% of oil, in literature 44.63% [9]. Whereas other cultivars – 37±0.05%.

The total amount of phenolic compounds

It should be noted that rapeseed itself contain more phenolic substances than any other major oilseed but it is not clear whether they are transferred from seed to oil or not (18). In this instance TPC was measured in the oil. It was found that exists strong correlation between TPC and IP, r=0,94. Yellow-seeded *Nex180* and *Holiday* cultivars had TPC for the most part, table 2 (843 and 605mg/100g of oil). These strains were the most stable (12.71h and 8.59h respectively).

Table 2. The oxidative stability and the total amount of phenolic compounds of divers cultivars of rapeseed oil

	IP,h	TPC, mg/100g
Sunday	5.99	332
Landmark	5.33	172
Ural	6.16	229
Kasimir	5.18	103
Heros	5.82	228
Casino	3.73	74
Pastel	5.86	244
Terra	5.94	342
Hendrix	5.54	275
Holiday	8.59	605
Nex180	12.71	843
Paladium	6.98	230
Prima	6.61	329
Senator	6.84	288
Rodeo	5.47	167

Conclusions

Studied 15 rapeseed cultivars grown in Lithuania are suitable to produce the edible oil because of determined small amounts (average 0.11%) of erucic FA. In the EU the amount of erucic FA in an edible rapeseed oil is limited to 2%.

In order to explain the good stability of rapeseed oil considerable amounts of oleic fatty acid were found (average 65.39%)[19]. Particularly in yellow-seeded rape. Yellow-seeded *Nex180* and *Holiday* cultivars were stable at 110°C temperature for 12.71h and 8.59h. It should be pointed out that *Sunday*, *Ural* and *Rodeo* are sorts which have quite high oxidative stability (IP=5.99h, IP=6.16h IP=5.47h respectively) parallel with MUFA (67.46%, 69.12%, 66.21%).

The ratio of linoleic and of α-linolenic fatty acid is approximately 2:1. As alluded to above, this is the needful ratio for a nutritional equilibrium. Higher MUFA and lower amounts of PUFA improved the oxidative stability as well [18, 19]. The correlation coefficents between oleic FA and IP was 0.76, between TPC and IP it was 0.94.

The best kinds of rapeseed are yellow-seeded *Nex180* and *Holiday*. They are the most oxidatively stable. It is mainly under the influence of huge amounts of MUFA. Despite the fact that the correlation coefficient was stronger between TPC and IP, it could be fallacious to conclude that TPC settles high IP. Just TPC assay may not be a suitable candidate of IP confirmation for measuring an antioxidant capacity because there are many other methods to estimate it [18] Furthemore, rapeseed oil has variety of other active compounds like tocopherols, sterols and etc. which were not analysed [19].

References

[1] United States Department of Agricultural, 21 June, 2006. Foreign Agricultural Service, Commodity Intelligence „Report Biodiesel Demand Continues Pushing Rapeseed Area up in The EU". USA, 21 June, 2006.

[2] Rashid U., Anwar F. 2008. Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil. Fuel, 87, 265-273.

[3] San Jose´ Alonso J., Lo´pez Sastre J.A., Romero-A´vila C., Lo´pez Romero E. J. 2006. Combustion of rapeseed oil and diesel oil mixtures for use in the production of heat energy. Fuel Processing Technology, 87, 97-102.

[4] Brown Lester R. 2006. Plan B 2.0: Rescuing a Planet Under Stress and a Civilization in Trouble, ISBN: 978-0-393-32831-8, W.W.Norton and Company.

[5] Gunstone D. 2004. Rapeseed and Canola Oil – Production, Properties and Uses. Frank Blackwel Publishing, CRC Press, Oxford (UK). XII + 222.

[6] Lynne Brown J. 2008. „Questions and answers about Canola oil", The Pennsylvania State University.

[7] Johnson S.P. 1977. Erucic acid in rapeseed oil. Food and Cosmetics Toxicology, 15(4), 348-353

[8] US Congress, 1991. Agricultural Commodities as Industrial Raw Materials, OTA-F-476. Office of Technology Assessment, US Government Printing Office, Washington, DC, 77.

[9] Wittkop, B., Snowdon, R. J., & Friedt, W. 2009. Status and perspectives of breeding for enhanced yield and quality of oilseed crops for Europe. Euphytica, 170, 131-140.

[10] Unal H., Sincik M., Izli N. 2009. Comparison of some engineering properties of rapeseed cultivars. Industrial Crops and Products, 30, 131-136.

[11] Kuprienė R. 2006. Development of yellow-seeded rapeseed (*Brasica Napus L.*) by biotechnological and classical breeding methods, Lithuanian University of Agricuture.

[12] Braipson-Danthine S., Gibon V., Deroanne C. 2005. Physicochemical characteristics of ternary fat blends involving low-erucic rapeseed oil. European Journal of Lipid Science and Technology 107, 627-633.

[13] Dubois V., Breton S., Linder M., Fanni J., Parmentier M. 2007. Fatty acid profiles of 80 vegetable oils with regard to their nutritional potential. European Journal of Lipid Science and Technology, 109, 710-732.

[14] Matthäus B., Brühl L. 2008. Why is it so difficult to produce high-quality virgin rapeseed oil for human consumption? European Journal of Lipid Science and Technology, 110, 611-617.

[15] Junker R., Kratz M., Neufeld M, Erren M., Nofer J. R., Schulte H., Nowak-Gottl U., Assmann G., Wahrburg U. 2001. Effects of diets containing olive oil, sunflower oil, or rapeseed oil on the hemostatic system. Journal of Thrombosis and Haemostasis, 85, 280-286.

[16] Trojakova L., Reblova Z., Pokorny J. 1999. Determination of the Oxidative Stability of Fats and Oils Using the Oxipres Apparatus. Journal of Food Science, 17(2) 68-72.

[17] Köckritz A., Martin A. 2008. Oxidation of unsaturated fatty acid derivatives and vegetable oils. European Journal of Lipid Science and Technology, 110, 812-824.

[18] Nakbi A., Issaoui M., Dabbou S., Koubaa N., Echbili A., Hammami M., Attia N. 2010. Evaluation of antioxidant activities of phenolic compounds from two extra virgin olive oils. Journal of Food Composition and Analysis 23, 711–715

[19] Kamal-Eldin A. 2006. Effect of fatty acids and tocopherols on the oxidative stability of vegetable oils. European Journal of Lipid Science and Technology, 58, 1051-1061.