Pol. J. Environ. Stud. Vol. 21, No. 3 (2012), 719-723

Original Research

Effect of Storage Period on Physicochemical Properties of Rapeseeds and Oil

Agnieszka Sujak[1]*, Magdalena Kachel-Jakubowska[2]

[1]Department of Physics, University of Life Sciences in Lublin, Poland
[2]Department of Machinery, Agricultural Exploitation and Management in Agricultural Engineering, University of Life Sciences in Lublin, Poland

Received: 22 June 2011
Accepted: 6 December 2011

Abstract

The physicochemical parameters of rapeseeds stored under laboratory conditions for up to 3 years were measured by spectroscopic techniques. Humidity, crude fat, sulphur-containing species in seeds and levels of carotenoids and chlorophylls in oils were assigned. For most of the seeds the minimal technological quality requirements were met. Lipid oxidation products in oils were estimated by the levels of the end products of lipid peroxidation. Interestingly, the oxidation of the lipids was not higher in the oils pressed from older seeds. In conclusion, the material stored for a long period is a valuable product for further processing.

Keywords: rapeseed, oil quality, physicochemical parameters

Introduction

Oil crops [1] and mainly rapeseed are one of the most important sources of feed and energy in Europe. The plant is estimated to be significant as a valuable material for processing in different branches of industry, mainly because it is a renewable source producing no water pollution, its production is easy, and it can be a new income source for agriculture [2]. Nutrition properties together with attractive color and thermal stability of rapeseed oils used for roasting are important factors determining oil usability in the food industry [3]. Carotenoids are responsible for the attractive colour of oil and are assumed to play a significant role in protection against attacks by free radicals, while chlorophylls are technically undesirable due to the unattractive smell and the visual darkening of the oils [4]. During the past decade a massive range of experiments has been conducted on glucosinolates that, similar to carotenoids, may act as antioxidants and serve as a good source of nutraceuticals [5-7]. In the case of the fuel industry the required raw material should be characterized by a low content of pigments, stable oil composition, and relatively high thermal stability [8-10].

In the present work we made an attempt to classify the rapeseed material stored over long periods by physicochemical parameters in order to estimate the most adequate starting condition features for further processing.

*e-mail: agnieszka.sujak@up.lublin.pl

Materials and Methods

Experimental Material

Experimental material consisted of 0.5 kg samples of industrial rapeseeds from the Oil Plant in Bodaczów, taken randomly from the bulk raw material supplied by 17 different contractors (marked in lines from 1 to 17). All the samples were from the Lublin area (southeastern Poland) and consisted of a mixture of different varieties of winter seeds (Bazyl, Bojan, Californium, Cabriolet, Casoar, Kaszub, Lisek, and Libomir) collected by individual suppliers. These cultivars are registered in The National Catalogue of

Table 1. Physicochemical parameters of the rapeseeds determined from the seeds from 17 different contractors stored for 1, 2, or 3 years.

	1			2			3		
Sample	Humidity [%]	Crude fat [%]	S-species [%]	Humidity [%]	Crude fat [%]	S-species [%]	Humidity [%]	Crude fat [%]	S-species [%]
1	6.69	44.58	8.13	8.14	41.87	14.65	7.05	42.23	11.95
2	6.71	41.99	13.48	7.99	42.51	11.04	6.49	43.08	9.95
3	7.03	41.39	13.02	8.04	42.07	11.41	7.15	43.25	10.95
4	7.18	43.45	10.14	8.14	41.78	11.72	7.08	42.42	10.64
5	7.15	43.39	10.92	7.48	42.30	12.57	6.70	43.28	10.52
6	6.90	42.05	11.15	7.39	42.68	13.22	7.45	42.10	11.04
7	6.82	41.94	13.83	6.93	42.25	11.91	7.23	41.68	12.65
8	6.57	44.11	8.49	7.44	43.06	11.71	6.78	42.28	10.75
9	6.91	42.91	11.42	6.60	41.11	11.81	7.25	42.49	12.78
10	7.23	42.79	11.05	7.91	42.99	10.11	7.39	42.32	11.84
11	6.81	41.98	13.82	7.80	41.50	12.83	7.33	41.68	11.57
12	7.43	41.36	12.50	9.40	42.67	10.31	6.46	41.69	11.32
13	6.91	41.84	12.07	7.73	42.81	10.44	7.02	42.51	12.37
14	7.33	42.18	10.93	7.38	44.03	10.48	7.39	41.19	11.05
15	7.28	41.98	12.83	7.55	43.12	8.62	7.23	43.08	12.60
16	7.22	42.97	10.48	7.33	42.36	12.91	6.11	42.69	11.69
17	6.56	43.35	12.11	7.64	42.24	11.81	6.95	42.89	10.94
Mean±S.D.	6.98±0.27	42.6±0.94	11.55±1.67	7.70±0.60	42.43±0.69	11.62±1.41	7.00±0.39	42.40±0.61	11.45±0.83

The obtained values are the arithmetic mean from 3 independent measurements under the condition that the admissible error was not higher than 0.5% of the measured value.

Agricultural Plant Varieties and also in the Common Catalogue of varieties of Agricultural plant species as PL 619, PL 611, PL 554, PL 554, PL788, and PL 205 [11]. Seeds were collected according to PN-EN ISO 542/1997 standard and stored under laboratory conditions at 19- 22ºC and 60-70% humidity for 1, 2, or 3 years (samples were marked in columns as 1, 2, or 3, respectively). Rapeseed oil was pressed on a laboratory pressing stand using a HYBREN 6 worm extruder equipped with micrometric mesh strainers. The process of pressing started after stabilization of the press temperature. After pressing of c.a. 1.5 kg of raw material the temperature of extruder reached 70ºC. The temperature was measured with a TP6 laser pyrometer. Oil was stored at 5ºC until used for analysis.

Physicochemical Characteristics of the Rapeseeds

Humidity, crude fat and sulphur-containing species (S-species) of the rapeseeds (in %) were determined using an Omega 10 UV-Vis-NIR Bruins Analyzer equipped with 10 interference filters for organic substances. The instrument was provided with internal standard for the rapeseeds. The obtained value was the arithmetic mean from 3 independent measurements under condition that the admissible error was not higher than 0.5% of the measured value.

Determination of Chlorophylls and Carotenoids

Chlorophylls and carotenoids were determined spectrophotometrically in the freshly pressed oil using a double-beam Varian Model Cary 300 Bio spectrophotometer. Samples of oils were diluted 5x in acetone and the spectrum measured between 350 and 700 nm. Concentrations of chlorophylls *a* (chl_a) and *b* (chl_b) and total carotenoids (Car) in µg/ml from 3 independent samples were calculated according to the procedure of Lichtenthaler and Buschmann [12].

Determination of Products of Lipid Peroxidation (TBARS)

Oils were subjected to thermal-induced oxidation. Oils in ceramic vials were heated at 125ºC. Freshly pressed oil was used as control. TBARS assay was used to assess lipid peroxidation using the method of Bar-Or et al. [13],

Table 2. Chlorophyll and carotenoid content of the seeds from 17 different contractors stored for 1, 2, or 3 years.

	1			2			3		
Sample	Chl_a (mg/ml)	Chl_b (mg/ml)	Car (mg/ml)	Chl_a (mg/ml)	Chl_b (mg/ml)	Car (mg/ml)	Chl_a (mg/ml)	Chl_b (mg/ml)	Car (mg/ml)
1	3.03±0.09	0.68±0.19	4.34±1.17	3.94±0.08	1.19±0.17	5.55±0.24	1.92±0.10	0.49±0.08	4.54±0.06
2	3.99±0.33	0.78±0.48	6.65±0.88	1.20±0.23	0.28±0.13	3.45±0.41	1.62±0.25	0.09±0.09	6.29±0.43
3	7.01±0.26	2.78±0.05	4.96±0.89	4.32±0.66	0.97±0.17	5.33±0.22	2.92±0.15	0.63±0.33	4.81±1.15
4	1.74±0.15	1.06±0.26	4.67±0.29	0.63±0.11	0.20±0.18	3.00±0.72	4.18±0.18	0.81±0.13	8.01±0.54
5	5.27±0.37	2.01±0.36	4.74±0.89	4.98±0.15	0.63±0.13	6.16±1.06	2.19±0.12	0.43±0.06	6.17±0.61
6	2.84±0.36	1.23±0.07	4.87±0.58	2.45±0.14	0.66±0.12	4.80±0.04	2.69±0.03	0.27±0.05	5.94±0.07
7	2.99±0.24	2.28±0.37	5.01±0.33	3.08±0.35	0.71±0.13	5.43±0.76	2.57±0.04	0.44±0.37	6.97±0.95
8	7.50±0.22	3.04±0.08	3.97±0.39	6.08±0.22	1.14±0.10	4.73±0.09	2.31±0.26	0.49±0.11	4.70±0.11
9	3.14±0.10	0.80±0.42	6.74±0.64	1.37±0.20	0.27±0.13	3.55±0.31	2.10±0.04	0.39±0.12	5.68±0.28
10	3.19±0.19	0.49±0.08	8.06±0.83	3.36±0.26	0.60±0.08	5.42±0.55	3.55±0.16	0.59±0.36	6.62±0.14
11	4.78±0.03	1.34±0.33	5.62±0.37	4.79±0.35	1.13±0.09	6.62±0.03	2.74±0.04	0.44±0.07	6.92±0.17
12	4.75±0.42	1.08±0.20	6.33±0.53	4.36±0.82	0.83±0.36	5.90±1.44	3.44±0.26	0.67±0.02	7.72±1.37
13	3.49±0.19	0.71±0.17	6.96±0.55	2.58±0.09	0.48±0.07	4.47±0.25	2.36±0.08	0.41±0.08	5.00±0.16
14	6.91±0.35	1.32±0.24	7.67±0.34	3.14±0.33	0.45±0.12	6.03±0.30	1.49±0.23	0.15±0.13	5.70±0.17
15	4.17±0.10	1.05±0.13	6.18±0.58	3.70±0.11	0.60±0.12	6.63±0.22	2.17±0.09	0.24±0.18	5.45±0.57
16	5.44±0.33	1.30±0.26	5.65±0.48	2.98±0.38	0.61±0.29	6.28±0.50	3.11±0.31	0.43±0.31	6.06±1.14
17	2.49±0.09	0.61±0.11	6.11±0.31	2.31±0.43	0.49±0.16	4.06±0.19	3.26±0.26	0.58±0.13	6.77±0.42
Mean±S.D.	4.28±1.69	1.33±0.76	5.80±1.21	3.25±1.44	0.66±0.30	5.14±1.13	2.62±0.72	0.44±0.19	6.08±1.02

with a few modifications. The total volume of reaction mixture was 1.57 ml and contained 0.14 ml 5N HCL, 0.28 ml of 40% trichloroacetic acid (TCA), 1.11 ml of 0.5% thiobarbituric acid (TBA) and 25 µl of oil sample and vortexed for 1 min. The ethanol solution of butylated hydroxytoluene (BHT) was added to the sample at a final concentration of 0.01%. Samples were heated for 10 min on a boiling water bath and then cooled to room temperature. A double-beam spectrophotometer was applied to measure the absorption spectrum between 400 and 600 nm. The baseline contained all the reaction components apart from oil. The absorbance difference between 600 and 535 nm was used as a TBARS value. The value of molar extinction coefficient $1.56 \cdot 10^5$ $M^{-1} \cdot cm^{-1}$ was used for calculations [13]. Measurements were done in three repetitions.

Statistical Analysis

The mean values ±S.D. (standard deviation) for all the determined parameters were calculated. The differences between the mean values were investigated using t-student test ($P \geq 0.05$). The analysis of correlation between the experimental data was performed using standard methods supplied with the MS Excel 2003 Analysis Tool Pack.

Results and Discussion

Table 1 shows the physicochemical parameters of the raw rapeseeds. For all the seeds except 2 samples the technological quality requirements for the 6-8% level of humidity and minimal content of crude fat were met [14, 15]. No statistical differences in humidity and crude fat was found between the samples stored for periods up to 3 years. The obtained content of sulphur-containing species (with glucosinolates) in seeds accounts for the amount lower than 25 µg/g of oil, which is the level required under current requirements (estimated by gas chromatography; unpublished report from laboratory of Oil Plant in Bodaczów).

On one hand, high glucosinolate content is a negative feature. On the other hand, glucosinolates are extensively examined for their bioactive actions such as antioxidant and anti-cancer activity [7]. As seen from our experiments, the level of sulphur-containing species stays unchanged even when relatively long storage times are applied. This gives useful information, that in spite of improper quality for food industry, the seeds can be used as a source of nutraceutical substances [5-7, 16].

Table 2 shows the detailed analysis of carotenoid and chlorophyll content in oils. Samples were characterized by a differentiated content of chlorophylls and carotenoids.

Table 3. Oxidation levels measured as the content of tiobarbituric acid-reactive lipid-oxydation species (TBARS) in rapeseed oils from 17 different contractors after 1, 2, or 3 years. All values expressed in mol × 10^{-5}/l of oil.

Sample	TBARS × 10^{-5} (mol/l)								
	1			2			3		
	0h	3h	6h	0h	3h	6h	0h	3h	6h
1	2.03±0.15	6.53±0.47	7.95±0.17	2.15±0.78	6.14±0.12	6.74±0.13	2.00±0.13	5.69±0.37	7.08±0.25
2	2.27±0.32	6.37±0.31	5.79±0.18	1.85±0.33	6.92±0.06	6.94±0.48	2.16±0.29	5.37±0.46	6.72±0.31
3	2.36±0.53	5.40±0.32	6.47±0.54	1.80±0.42	4.77±0.08	5.43±0.11	2.41±0.18	5.42±0.36	6.68±0.42
4	2.45±0.34	8.18±0.68	9.36±0.22	2.78±0.40	7.25±0.01	10.30±0.88	1.45±0.31	4.97±0.37	6.31±0.26
5	2.28±0.25	4.41±0.58	7.68±0.93	2.80±0.34	9.44±0.08	9.94±0.54	2.10±0.12	5.31±0.34	6.91±0.23
6	2.59±0.43	6.32±0.98	7.91±0.26	0.86±0.09	8.81±0.26	9.90±1.01	1.89±0.27	5.74±0.43	6.46±0.25
7	4.41±0.83	5.48±0.46	7.11±0.57	3.58±0.83	7.77±0.41	8.26±0.74	1.64±0.12	6.61±0.20	7.84±0.17
8	3.73±0.48	7.91±0.89	7.92±0.34	3.12±0.83	6.66±0.13	6.97±0.18	2.02±0.05	5.78±0.16	6.13±0.48
9	2.98±0.87	7.18±0.18	6.92±0.47	2.51±0.51	7.96±0.27	9.54±0.88	2.08±0.11	5.42±0.23	5.82±0.18
10	1.95±0.41	7.05±0.82	7.24±0.28	2.23±0.16	5.46±0.37	6.95±0.05	1.38±0.08	6.85±0.16	6.55±0.26
11	2.34±0.52	6.03±0.16	7.38±0.16	3.00±0.64	6.68±0.36	7.69±0.35	2.09±0.09	5.70±0.69	7.06±0.23
12	2.69±0.52	4.25±0.24	5.37±0.89	1.98±0.13	4.86±0.41	6.27±0.60	3.14±0.14	5.59±0.46	6.99±0.23
13	1.92±0.83	6.11±0.16	8.77±0.44	1.84±0.09	7.79±0.45	8.89±0.85	2.52±0.32	4.89±0.09	6.14±0.83
14	2.67±0.36	7.05±0.38	10.30±0.67	1.95±0.14	8.19±0.42	10.80±0.73	2.14±0.16	5.44±0.33	7.75±0.18
15	2.79±0.33	6.94±0.82	11.70±0.99	2.79±0.28	8.45±0.19	9.99±0.48	2.14±0.08	5.32±0.28	7.35±0.26
16	3.43±0.28	9.04±0.55	11.2±1.03	1.93±0.41	8.07±1.01	7.47±1.22	1.78±0.08	5.32±0.15	4.39±0.33
17	3.37±0.56	6.98±0.43	9.79±0.17	2.73±0.46	6.73±0.75	7.92±0.59	2.27±0.15	5.6±0.23	6.14±0.34
Mean±S.D.	2.72±0.68	6.52±1.25	8.07±1.80	2.35±0.65	7.17±1.34	8.24±1.61	2.07±0.64	5.59±0.48	6.61±0.81

Neither statistical differences between oils nor statistical correlation between the data obtained for the carotenoid content were observed (at $P \geq 0.05$) within the groups of samples. In spite of prolonged storage time the level of carotenoids remained constant within the experimental error, while the level of chlorophylls decreased and was statistically different between the groups of oils from the seeds kept for 1, 2, or 3 years ($P \geq 0.05$). This may be of interest for the producers of edible oils, where a possibly low chlorophyll content is required. This depends on many factors, among which is the effect of cultivar, the harvesting of the seeds before full technical maturity and also storage conditions [3-4, 16-18]. Of importance also is the other post-cropping process such as drying temperature [15, 19]. In general, carotenoids are considered to act as antioxidants and act as lipid protectors as well as vitamin precursors. The thermal stability of oils has been assessed by measuring the levels of malonaldehyde – lipid oxidation precursor (called TBARS; data shown in Table 3). Interestingly, the oxidation of the lipids in oils was not higher in the oils pressed from the seeds stored over long periods. The initial amounts of TBARS were close to the c.a. $2.5 \cdot 10^{-5}$ mol/l of oil. On the contrary, the tendency of TBARS value to decrease was observed. The initial level of TBARS was not correlated with the levels of carotenoids or chlorophyll, and additionally there was no statistical correlation between samples containing higher amounts of carotenoids with the TBARS concentration after 3 or 6h of thermal degradation. For samples stored for 1 or 2 years the negative correlation between the initial level of TBARS and levels of sulphur-containing species, carotenoids, and chlorophylls was found, while no correlation was found for the samples stored for 3 years, which indicates that the process of oil oxidation is more complex and that carotenoids do not act as straightforward antioxidants as in model lipid membranes [20, 21]. Interestingly, oils from older seeds were, in most cases, thermally more stable.

Although in many cases seeds show a relatively high technological value, the wide-scale production of goods from rapeseed stored for longer periods is strongly dependent on the costs of seed drying and storage.

References

1. VELDE M., BOURAOUI F. European biodiesel production: current and future environmental impacts of rapeseed cultivation at pan-European scale. Geophysical Research Abstracts 10, **2008**.

2. EU COMMISION. Biofuels in the European Union: an agricultural perspective. Fact Sheet 1, **2006**.
3. TYS J., SUJAK A., BOGDAN A. Changes to the composition of colorants caused by the temperature of drying rapeseed. Int. Agrophysics **16**, 307, **2002**.
4. TYS J., SUJAK A., RYBACKI R. Drying temperature-induced changes of the seed pigment components of the Winter oilseed rape. Oilseed Crops **XXIII**, 95, **2002** [In Polish].
5. JOHNSON I.T. Glucosinolates: bioavailability and importance to health. Int. J. Vitam. Nutr. Res. **72**, (1), 26, **2002**.
6. PALMIERI S. Glucosinolates nutraceutical product? Agro-Food Ind. Hi-Tech. **7**, 1, **2000**.
7. CHUANPHONGPANICH S., PHANICHPHANT S., BHUDDASUKH D., SUTTAJIT M., SIRITHUNYALUG B. Nutraceutical and Functional Food. J. Sci. Technol. **28**, 55, **2006**.
8. KRIČKA T., VOĆA N., JANUŠIĆ V., TOMIĆ F., JUKIĆ Z, MATIN A. Influence of treatment and storage of rapeseed on its properties as a raw material for biodiesel production. Agriculturae Conspectus Scientificus **72**, (3), 173, **2007**.
9. OSEK M. Influence of storage time and conditions on changes in lipid fraction of some rapeseeds products. Oilseed Crops **XXI**, 145, **2000** [In Polish].
10. JACKOWSKA I., TYS J. Factors Determining the Usefulness of Rapeseed in the Production of Biofuels. Pol. J. Environ. Stud. **3A**, 76, **2007**.
11. CCA (Common Catalogue of varieties of Agricultural plant species) C, 179, **2010**.
12. LICHTENTHALER H.K., BUSCHMANN C. Chlorophyll and Carotenoids: Measurement and Characterisation by UV-Vis Spectroscopy. In: Current Protocols in Food Analytical Chemistry S1, F4.3.1., **2001**.
13. BAR-OR D., RAEL L.T., LAU E.P., RAO N.K., THOMAS G.W., WINKLER J.V., YUKL R.L., KINGSTON R.G., CURTIS C.G. An analog of the human albumin N-terminus (Asp-Ala-His-Lys) prevents formation of copper-induced reactive oxygen species. Biochem. Biophys. Res. Commun. **284**, 856, **2001**.
14. PSZCZOŁA J. Good seed- good yield, good rapeseeds the shooter. Rape-biofuels. A Guide for Producers. Business Press, Warsaw, Poland. **2006** [In Polish].
15. KACHEL-JAKUBOWSKA M., SZPRYNGIEL M. Influence of drying condition on quality of rapeseed. Int. Agrophysics **22**, 327, **2008**.
16. TAŃSKA M., ROTKIEWICZ D. Different factors influencing rapeseed quality. Oilseed Crops **XXIV**, 709, **2003** [In Polish].
17. STROBEL W., TYS J., SUJAK A., GAGOŚ M., ŻAK W., KOTLARZ A., RYBACKI R. Harvesting technique versus the content of chlorophylls and carotenoids in rape seeds, oilcakes and rapeseed oil. Oilseed Crops **XXVI**, 479, **2005** [In Polish].
18. FAHEY J.W., ZALCMANN A.T., TALALAY P. The chemical diversity and distribution of glucosinolates and isothiocyanates among plants. Phytochemistry **56**, 5, **2001**.
19. BRLEK SAVIĆ D., KRIČKA T., VOĆA N., JURIŠIĆ V., MATIN A. Effect of Storage Temperature on Rapeseed Quality. Agriculturae Conspectus Scientificus **74**, (3), 143, **2009**.
20. SUJAK A., GABRIELSKA J., GRUDZIŃSKI W., BORC R., MAZUREK P., GRUSZECKI W.I. Lutein and Zeaxanthin as protectors of Lipid Membranes against Oxidative Damage: The Structural Aspects. Arch. Biochem. Biophys. **371**, (2), 301, **1999**.
21. McNULTY H.P., BYUN J., LOCKWOOD S.F., JACOB R.F., MASON R.P. Differential effects of carotenoids on lipid peroxidation due to membrane interactions: X-ray diffraction analysis. Biochim. Biophys. Acta **1768**, 167, **2007**.