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Effects of different roasting conditions on the nutritional value and oxidative stability of high-oleic and yellow-seeded *Brassica napus* oils

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SUMMARY: This study was conducted to evaluate the possibility of enhancing the nutritional value and oxidative stability of rapeseed oil obtained from seeds subjected to thermal treatment prior to pressing. The yellow-seeded and high-oleic *B. napus* lines, harvested in Poland, were roasted prior to pressing for 1 h at 100 and 150 °C. This study highlighted how rapeseed breeding lines affect the quality profile of the oils obtained both before and after the roasting process. In principle, the high-oleic *B. napus* was accompanied by a nearly 2-fold increase in oxidative stability compared to the yellow-seeded *B. napus*, most likely due to a higher content of oxidation-resistant oleic fatty acids (~74.24% vs. ~60.76%) and a decreased concentration of oxidizable PUFAs (~16.32% vs. ~31.09%). Similar to the case of roasting black-seeded rapeseed, the thermal pre-treatment of yellow-seeded and high-oleic *B. napus* prior to pressing did not alter the composition of their fatty acids. Based on the results obtained in this study, it can be concluded that roasting seeds prior to pressing does not reduce the amount of tocopherols in the oil; moreover, a slight increase in γ-tocopherol content was observed.

KEYWORDS: *Fatty acids; High-oleic* B. napus; *Rapeseed oil oxidative stability; Roasting conditions; Tocopherols; Yellow-seeded* B. napus

RESUMEN: ***Efecto de diferentes condiciones de tostado sobre el valor nutritivo y la estabilidad oxidativa de aceites de semillas de*** **Brassica napus** ***alto oleico y semillas amarillas.*** Este estudio se realizó para evaluar la posibilidad de aumentar el valor nutritivo y la estabilidad oxidativa del aceite de colza obtenido a partir de semillas sometidas a tratamiento térmico antes del prensado. Las líneas de *B. napus* sembrados amarillos y alto oleico, cosechadas en Polonia, fueron tostadas antes de ser prensadas durante 1 hora a 100 y 150 °C. Este estudio pone de relieve cómo las líneas de colza mejoradas ven afectado el perfil de calidad de los aceites obtenidos antes y después del proceso de tostado. En principio, el alto oleico *B. napus* aumenta casi 2 veces la estabilidad a la oxidación en comparación con semilla amarilla *B. napus*, muy probablemente debido a un mayor contenido de ácido graso oleico resistente a la oxidación (~74,24% vs. ~60,76%) y una concentración menor de PUFAs oxidables (~16,32% frente a ~31,09%). Similar al caso de tostar semillas de colza-negro, las semillas amarillas y las alto oleico de *B. napus* antes tratadas térmicamente antes del prensado no alteran su composición de ácidos grasos. También Basándonos en los resultados obtenidos en este estudio, se puede concluir que el tostado semillas antes del prensado no reduce la cantidad de tocoferol en aceite; Además, se observó ligero aumento en el contenido de γ-tocoferol.

PALABRAS CLAVE: *Aceite de colza; Ácidos grasos; Alto oleico* B. napus; *Condiciones de tostado; Estabilidad oxidativa; Semillas amarillas* B. napus; *Tocoferoles*

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1. INTRODUCTION

Rapeseed (*Brassica napus*) is the third most important oilseed crop in the world after palm oil and soybean and the most cultivated oilseed in Poland. Rapeseed oil is considered one of the healthiest cooking oils, particularly due to its beneficial balance of fatty acids. It is low in saturated fatty acids (<7%), it contains a high content of monounsaturated fatty acids in the form of oleic acid (58.0–62.0%) and it is a good source of α-linolenic (C 18-3) ω-3 fatty acid (8.0–12.0%). Moreover, rapeseed oil contains a nutritionally favorable linoleic (ω-6) to α-linolenic (ω-3) essential fatty acids ratio of 2:1 (O'Brien, 2008). The physical and chemical properties of vegetable oils can be modified through the genetic modification of oilseeds such as canola, soybean, corn and sunflower. Modifying the fatty acid composition by decreasing the amount of oxidizable fatty acids such as α-linolenic and linoleic acids and increasing the amount of oxidation-resistant fatty acids such as oleic acid improved the oil's oxidative stability (Merrill *et al*., 2008). Such enhancement of a genetically diverse gene pools is an essential plant breeding requirement. Yellow-seeded rapeseed strains from inter-specific crosses represent a potentially important genetic diversity expansion resource in the gene pool of *B. napus*, since it was reported that the yellow-seed line contains significantly more oil and protein as well as less total dietary fiber than black-seeded lines (Burbulis and Kott, 2005).

According to the Codex Alimentarius Standard for Named Vegetable Oils (Codex Stan 210-1999) oils "obtained, without altering the nature of the oil, by mechanical procedures, e.g. expelling or pressing, and the application of heat only" are defined as "virgin oils". The thermal pre-treatment of oilseeds is one of the most important processing steps in oilseed processing. The purpose of this step is to damage the oil cells in order to obtain a temperature-dependent decline of oil viscosity along with improved fluidity of the oil, and to optimize the moisture content of the seeds for further processing. As a consequence, such effects improve screw-pressing capacity, cake formation and facilitate the extractability of the oil. In addition, the inactivation of seed-specific enzymes and disinfection of the seeds by eliminating adhering fungi and bacteria are of great importance (Matthäus, 2012). The heat treatment of rapeseed prior to pressing has been reported to vastly improve the oxidative stability of oil due to an improved extractability of components with antioxidative capacity such as tocopherols, phenols, phospholipids, Maillard reaction products and sterols (Prior *et al*., 1991a,b; Wijesundera *et al*., 2008; Kraljić *et al*., 2013).

The changes in quality which occur during the roasting process prior to the pressing of the black-seeded *Brassica napus* varieties, have been well investigated (Prior *et al*., 1991a,b; Górecka *et al*., 2003; Wijesundera *et al*., 2008; Kraljić *et al*., 2013); however, information on the application of the roasting process prior to pressing using yellow-seeded as well as high-oleic *B. napus* is scarce. The objectives of this research were: (1) to evaluate the effect of different roasting conditions on the changes in nutritional value of yellow-seeded and high-oleic *B. napus* oil, assessed in terms of changes in fatty acids composition, alteration of total tocopherols, pigment contents in the oil, and their influence on oil stability; (2) to investigate the effect of thermal pre-treatment prior to pressing on hydrolytic and oxidative changes occurring in the lipid fraction during roasting depending on the variety of rapeseed; and (3) to analyze the correlation between the roasting conditions and sensory quality of the oil.

2. MATERIALS AND METHODS

2.1. Materials

The yellow-seeded *B. napus* line PNz022 and high-oleic *B. napus* line PN 1170, developed at the Institute of Plant Breeding and Acclimatization–National Research Institute (Poznan, Poland) was used. The seeds were harvested at optimum maturity, and did not contain any impurities or broken seeds. They were stored in paper bags in atmospheric conditions at 15±2 °C.

2.2. Chemicals and solvents

Analytical standards of γ- and α-tocopherols (purity >95% by HPLC) were purchased from Sigma Aldrich (USA). HPLC-grade *n*-hexane, methanol (MeOH), acetonitrile (ACN), methyl *tert*-butyl ether (MtBE) and potassium hydroxide (KOH) were obtained from POCH (Poland). $FeCl_2$ >99% and NH_4SCN (ammonium thiocyanate) of HPLC purity were purchased from Merck (Germany). All other solvents and chemicals used in this study were acquired from Chempur (Poland) and Merck (Germany).

2.3. Roasting conditions and oil pressing parameters

For each sample, 1.5 kg of whole rapeseeds were thinly and evenly spread out on the bottom of a glass beaker tightly covered with aluminium foil and heated for 1 h inside an oven with forced ventilation (SUP-100, WAMED, 2600 W) maintained at a specified temperature (100 or 150 °C). To obtain a homogenous degree of roasting the seeds were stirred every 15 min. Oil pressing was carried out immediately after seed removal from the oven with the use of a screw press Farmer 10 (Farmet, Czech Republic), with a nozzle diameter of 8 mm. The temperature inside the press was set at 60±2 °C, and the temperature of the outflowing oil produced from unroasted rapeseed sample (control) was 38±1 °C.

Each experiment was performed in duplicate for every rapeseed variety. After pressing, the oils were filtered to remove particles, and then kept in dark glass bottles (vol. of 65 mL) under refrigeration temperature (4±2 °C) until analyzed.

2.4. Oil content

The oil content of seeds and cake was determined by automated Soxhlet extraction (Soxtec™ 2050 Auto Fat Extraction System). The samples (5 g) were weighed into thimbles and inserted into the extraction unit. Solvent (petroleum ether 40/60 pa) was added to the extraction cups in a closed system. The cups were heated by the electric heating plate. The 4-step extraction consisted of boiling, rinsing, evaporation/solvent recovery and pre-drying. Three repetitions were made for each measurement and the average data collected was used for statistical analysis. The dried samples were accurately re-weighed and the oil content in the seeds and cake was expressed as % of dry mass.

2.5. Moisture content

The moisture content of the seeds and cake was determined according to ISO, 2000 standard method. The measured mass loss was expressed as percentage of water content in the sample.

2.6. Oil yield

The oil yield was calculated on the basis of the following formula (Swetman and Head, 1998):

$$Y = 100 \times \frac{R_S}{R_C}$$

where: *Y*-oil yield, R_s-the ratio of non-lipid components in the seeds to the oil content in the seeds, R_c-the ratio of non-lipid components in the cake to the residual oil content in the cake. For each sample 2 measurements were taken.

2.7. Characteristic values

The characteristic values were determined according to the following ISO standard methods: acid value (AV) expressed in milligrams of potassium hydroxide necessary to neutralize the free acids in 1 g of sample (ISO, 2005), peroxide value (PV) expressed in mili equivalents of active oxygen·kg^{-1} of oil (ISO, 1996), anisidine value (*p*-AnV) expressed as the optical density measured at 350 nm, multiplied by 100 of the solution of 1 g of fat in 100 mL of *p*-anisidine (ISO, 2008), the TOTOX index, a combination of PV and *p*-AnV, expressed as a measurement of the total oxidation, including primary and secondary oxidation products (ISO, 2008). The conjugated dienes and trienes, expressed by the absorption coefficient $E_{1\ cm}^{1\ \%}$ at λ_{max} 232 and 286 nm, respectively, were determined using Thermo Spectronic Helios β spectrophotometer (ISO, 2011).

2.8. Fatty acid composition

A mass of 0.2 g of oil was weighed and dissolved in 2 mL of hexane. The mixture was submitted for saponification with 0.5 mL of a sodium hydroxide solution in methanol (2 M) at room temperature for 2 h. Then 200 µL of the hexane layer were transferred into a 1.5 mL auto sampler vial and dissolved in 1 mL of hexane. The diluted FAME (1 µL of the sample) were separated on a GC-MS system (Agilent 6890N GC, Agilent Technologies, USA) equipped with a BPX 70 capillary column (60 m length, 0.22 mm i.d., 0.25 µm film thickness) and flame-ionization detector (FID). Helium was used as a carrier gas at a flow rate of 1.5 mL·min^{-1}. The column temperature was programmed at 2 °C·min^{-1} with an initial temperature of 130 °C and final temperature of 235 °C. The injector was set at 230 °C with a split ratio of 100:1 and the detector was set at 250 °C. Fatty acids were identified by comparing their retention times with authentic standards, and the results were reported as weight percentages following integration and calculation using ChemStation (Agilent Technologies).

2.9. Tocopherols

A sample of 0.2 g of oil was dissolved in 5 mL of an ACN/MtBE mixture (4:6 by vol.). The mixture was filtered through a micro syringe filter (titan PTFE 0.2 lm). Then, 5 µL of the sample were injected into a VP Shimadzu HPLC system coupled with DAD detector (SPD-M10AVP, Shimadzu, Japan) and fluorescence detector (RF-10AXL, Shimadzu, Japan), reversed phase octadecyl silica Gemini C 18 column (150 mm×2 mm×3 µm) (Phenomenex Torrance, CA, USA) and suitable guard column. The isocratic mobile phase was a mixture of ACN and MtBE (4:6 v/v) at a flow rate of 0.15 mL·min^{-1}, and the column oven temperature was 35 °C. The tocopherols were detected by standard UV spectrum analysis (190–370 nm). Quantification of tocopherols was conducted using data from the fluorescence detector (FLD) with excitation/emission wavelengths of 290/330 nm, respectively. All samples were analyzed in triplicate and the tocopherol/oil ratio was expressed in mg·100 g^{-1}.

The vitamin E content, expressed in d-α-tocopherol equivalents (α-TE) was calculated by multiplying milligrams of α-T by 1.0 and γ-T by 0.1 (Eitenmiller and Lee, 2004).

The Harris coefficient, expressed as the ratio of α-tocopherol equivalent (mg) to the mass (g) of polyunsaturated fatty acids in 100 g of the oil, was calculated (Witting, 1972).

2.10. Pigments

Total carotenoid pigments, expressed as β-carotene, were assayed spectrophotometrically for oil samples diluted in cyclohexane at 445 nm (BSI, 1977), and the results were calculated in accordance with the formula:

$$\text{Total carotenoids} = \frac{383 \times A_{445}}{L \times c}$$

where: A_i is the absorbance of the oil at the respective wavelength (nm), L is the thickness of the spectrophotometer cell (mm), c is the concentration of the oil solution in cyclohexane (g·100 mL^{-1}).

The total chlorophyll pigments, expressed as pheophytin *a*, were determined according to the AOCS Method (1997) using the Thermo Spectronic Helios β spectrophotometer. The oil sample was placed in the 1 cm cell and the absorbance was read at a wavelength of 630, 670, and 710 nm. The results were calculated for the amount of total chlorophyll pigments according to the formula:

$$\text{Total chlorophylls} = 34.54 \frac{A_{670} - 0.5\ (A_{630} + A_{710})}{L}$$

where: where A_i is the absorbance of the oil at the respective wavelength (nm), L is the thickness of the spectrophotometer cell (mm).

2.11. Oxidative stability

According to ISO, 1997 the oxidative stability of the oils was determined with a Rancimat apparatus (Metrohm model 743; Metrohm KEBO Lab AB, Herisau, Switzerland). Oil samples were weighed (2.5 g) into the reaction vessel in quadruplicate and heated to 120 °C under an air flow of 20 $L \cdot h^{-1}$. The induction period (IP) was expressed in hours (h).

2.12. The sensory assessment of oils

Sensory evaluation was performed in duplicate with a selected, trained panel consisting of 10 persons in accordance with the ISO, 2003 standard. The oil samples (15 mL) were served in vessels at room temperature (20±2 °C). The sensory profile of the oils was determined in accordance with the reference sensory assessment of virgin rapeseed oils (Brühl and Matthäus, 2008). Nine flavor attributes, including seed-like, nutty, woody, bitter, roasted, burnt, rancid, fusty, musty were chosen. A quantitative sensory description was conducted using a graded 10-point scale to measure the intensity of attributes, ranging from zero ("not detectable") to ten ("intense"). In order to determine the degree of unstructured consumer acceptability, a continuous 10 cm length scale was used, marked with two verbal anchors: "like" and "dislike". The intensity of individual discriminates was expressed in arbitrary units (Baryłko-Pikielna and Matuszewska, 2009).

2.13. Statistical analysis

The data were subjected to Analysis of Variance (ANOVA) by applying Statistica 10 software. Significant differences among means were determined through Tukey's Multiple Range Tests. P values less than 0.05 were considered statistically significant.

3. RESULTS AND DISCUSSION

3.1. Effect of roasting conditions on oil extraction yield

The initial moisture and oil contents of the analyzed rapeseed varieties were as follows: 6.8 and 46.6% for high-oleic rapeseed, 5.3 and 35.5% for the yellow-seeded rapeseed variety, respectively (Table 1). Immediately after the roasting process the temperature reached by the seeds was measured. Figure 1 illustrates the changes in seeds and oil temperature in function of roasting temperature. The average temperature of the seeds heated at 100 °C was 60 °C, while the seeds roasted at 150 °C reached an average temperature of 88 °C. Because the oil was pressed immediately after roasting, the average temperature of the outflowing oil was in the range of 46.5 to 64.3 °C for the oil produced from 100 and 150 °C for roasted seeds, respectively. Along with roasting temperature elevation, the decrease in seed moisture content was observed. A slight decrease in the water content occurred during the roasting process conducted at 100 °C (3 to 4%), while the temperature elevation to 150 °C resulted in a 23 to even 30% loss in water content (Table 1). To investigate the effect of the roasting pre-treatment on the oil extraction yield, pressings were performed using roasted and unroasted samples. When high-oleic rapeseed samples were roasted at 100 °C no statistically significant increase in oil yield was observed ($p>0.05$), whereas elevating the temperature to 150 °C resulted in an increased oil yield by 18.3% compared to the untreated rapeseed samples. The amount of oil obtained from pressing yellow-seeded rapeseed after roasting the seed using temperatures between 100 °C and 150 °C was increased by 37.2–39.7% in comparison with cold-pressing. The above observation corresponds to data presented by Prior *et al.* (1991b), where rapeseed conditioning at 100 °C resulted in an oil yield increase of 20% compared to untreated rapeseed samples. Increased oil yield can be linked to the fact that temperature-dependent decline of oil viscosity, along with improved oil fluidity, occur during thermal pre-treatment of oilseeds, which facilitates the extraction of the oil and minimizes the quantity of the oil remaining in the oil cake (Matthäus, 2012).

TABLE 1. Moisture and oil content in the seeds and cake of rapeseed varieties used in the evaluation

Rapeseed variety		Roasting temperature (°C)	Oil content (%) $\bar{x}$±SD	Moisture content (%) $\bar{x}$±SD	Oil yield (%) $\bar{x}$±SD
High-oleic	seed	–	46.6±0.92^{a}	6.8±0.07^{a}	–
	cake	unroasted	23.41±0.31^{b}	6.8±0.41^{a}	63.6±0.06^{a}
		100 °C	23.45±0.53^{b}	6.5±0.81^{b}	64.9±0.41^{a}
		150 °C	18.25±0.47^{c}	5.2±0.22^{c}	75.3±0.23^{b}
Yellow-seeded	seed	–	52.2±0.25^{A}	5.3±0.36^{A}	–
	cake	unroasted	35.5±0.40^{B}	5.3±0.35^{A}	49.5±0.17^{A}
		100 °C	25.6±0.54^{C}	5.1±0.16^{B}	68.0±0.06^{B}
		150 °C	25.4±0.57^{C}	3.7±0.10^{C}	69.2±0.50^{B}

Mean values denoted by different letters in columns constitute a statistically significant difference at $p<0.05$; (n=2×2).

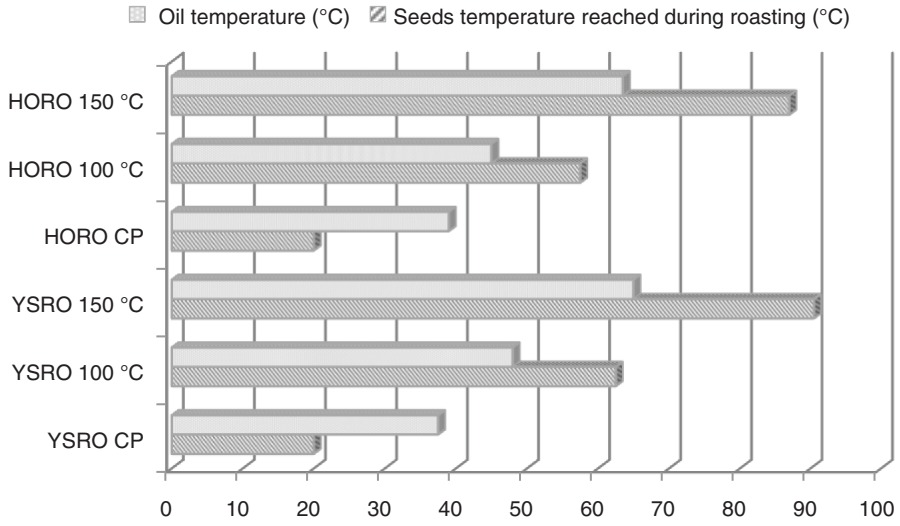

FIGURE 1. Seeds and oil temperature (°C) as a function of roasting temperature. Explanatory notes: HORO–high-oleic rapeseed oil; YSRO–yellow-seeded rapeseed oil; 100, 150 °C–roasting temperature; CP–cold-pressed.

3.2. Effect of roasting conditions on the degree of hydrolysis of oils

The acid value (AV) of the oils extracted from different rapeseed varieties is presented in Table 2. Cold-pressed oil obtained from high-oleic rapeseed was characterized by a much lower degree of hydrolysis (AV=0.42 mg KOH·g^{-1}) compared to yellow-seeded rapeseed oil (AV=1.66 mg KOH·g^{-1}), which may indicate inferior initial quality of the yellow-seeded *B. napus* seeds used in the evaluation. Roasting high-oleic rapeseed samples resulted in a practically unchanged (p>0.05) degree of hydrolysis, while roasting yellow-seeded rapeseed prior to pressing resulted in a statistically significant increase in the AV of the obtained oil. Nevertheless, the AV of all the oils did not exceed the limits specified in the Codex Alimentarius (≤4 mg KOH·g^{-1}) for cold-pressed and virgin oils (Codex Stan 201-1999). Górecka *et al*. (2003) found no significant changes in the AV when roasting rapeseed between 80 and 100 °C, while Wroniak *et al*. (2013) reported that roasting rapeseed at 150 °C resulted in an increased hydrolysis degree of the obtained oil.

3.3. Effect of roasting conditions on the degree of oxidation of oils

The average PV of oils extracted from seeds roasted at a temperature of 100 °C ranged from 1.04 to 1.59 mEq O_2·kg^{-1}, whereas increasing the temperature to 150 °C resulted in a nearly doubled (high-oleic rapeseed oil) and tripled (yellow-seeded rapeseed oil) increase in the PV compared to unroasted oil samples

TABLE 2. Quality parameters of rapeseed oils produced by cold pressing or pressing after roasting seeds

Rapeseed variety	Roasting temperature (°C)	Acid value (mg KOH/g)	Peroxide value (mEq $O_2 \cdot kg^{-1}$)	Anisidine value	TOTOX index	Dienes UV 232 nm	Trienes UV 268 nm	Induction period(h)
		$\bar{x}$±SD	$\bar{x}$±SD	$\bar{x}$±SD	$\bar{x}$±SD	$\bar{x}$±SD	$\bar{x}$±SD	$\bar{x}$±SD
High-oleic	unroasted	0.42±0.02^{a}	1.32±0.08^{a}	0.14±0.04^{a}	2.78±0.14^{a}	1.32±0.05^{a}	0.07±0.01^{a}	6.88±0.18^{a}
	100	0.46±0.03^{a}	1.59±0.03^{b}	0.40±0.09^{b}	3.57±0.13^{b}	1.86±0.02^{b}	0.11±0.01^{b}	7.24±0.20^{a,b}
	150	0.45±0.01^{a}	2.52±0.11^{c}	0.54±0.15^{b}	5.58±0.38^{c}	2.01±0.07^{c}	0.17±0.01^{c}	7.62±0.33^{b}
Yellow-seeded	unroasted	1.46±0.00^{A}	0.56±0.06^{A}	0.40±0.09^{A}	1.52±0.16^{A}	1.75±0.03^{A}	0.20±0.01^{A}	3.51±0.07^{A}
	100	1.66±0.03^{B}	1.04±0.10^{B}	0.87±0.13^{B}	2.95±0.11^{B}	1.76±0.09^{B}	0.22±0.00^{A}	3.69±0.05^{A}
	150	1.69±0.01^{B}	1.70±0.06^{C}	1.08±0.04^{B}	4.48±0.15^{C}	1.91±0.03^{B}	0.35±0.03^{B}	4.53±0.14^{B}

Mean values denoted by the same letter in the columns do not constitute statistically significant differences at $p<0.05$; (n=2×2).

(Table 2). Despite a statistically significant increase in PVs along with increased temperature, the level of primary oxidation products was within the Codex Alimentarius limits (PV <15 mEq $O_2 \cdot kg^{-1}$) (Codex Stan 201-1999), which indicates a small amount of oil oxidation during the thermal treatment of seeds. Consistent with these results, rapeseed roasting contributed to a significant increase in PVs in a study conducted by Prior *et al.* (1991a), Górecka *et al.* (2003), Kraljić *et al.* (2013), and Wroniak *et al.* (2013). Secondary oxidation products such as saturated and unsaturated carbonyl compounds of high molecular weight were measured as anisidine value (*p*-AnV). The results showed that the formation of secondary oxidation products was from 2-fold (100 °C) to even 3-fold (150 °C) higher in thermally treated rapeseed samples compared to untreated ones (Table 2), which is consistent with previously reported data (Górecka *et al.*, 2003; Wroniak *et al.*, 2013). The PV, in combination with *p*-AnV, is often used to determine the TOTOX index, which is considered a very suitable indicator of the oxidative quality of oils. The TOTOX index of all the examined oils did not exceed the limit of 10, specified for edible oils, indicating negligible changes during thermal pre-treatment of the lipid fraction of the seeds. Relative oxidation degree is quantified using changes in UV absorbance at 232 and 268 nm. The oxidation process of PUFAs occurs along with the formation of hydroperoxides, followed by a rearrangement of non-conjugated double bonds present in unsaturated lipids, which generates conjugated dienes (CD), which absorb at 232 nm. The presence of three or more double bonds in PUFA molecules results in the formation of conjugated trienes (CT), which absorb at 268 nm (Albi *et al.*, 1997). The content of dienes is a consequence of primary oxidation, whereas the presence of trienes indicates the formation of oxidation by-products such as unsaturated α-and β-diketones and β-ketones. The results presented in Table 2 show that there was a trend toward increasing the formation of CD and CT in line with increasing the roasting temperature, which was consistent with changes observed in the PV, taking into account the fact that these conjugated compounds are formed in parallel to the formation of hydroperoxides.

3.4. Effect of roasting conditions on the changes in fatty acid composition

The fatty acid composition of all the examined oil samples is described in Table 3. The oils produced using high-oleic rapeseed contained higher concentrations of oleic acid (18:1, 73.89–74.58% range), lower levels of linoleic acid (18:2*n-6*, 11.14–11.51% range) and α-linolenic acid (18:3*n-3*, 4.88–5.08% range) compared to yellow-seeded rapeseed (18:1, range 60.67–61.20%, 18:2*n-6*, 20.96–21.06% range, 18:3*n-3*, 9.98–10.11% range), exhibiting the typical composition of a 00-rapeseed fatty acid (Codex Stan 210-1999). The concentration of saturated fatty acids was low in all the analyzed samples and ranged from 6.04 to 6.36%. According to the sources, the oleic acid content in high-oleic canola oils ranged from 69 to 77% (approximately 60% of oleic acid in traditional rapeseed varieties), with linoleic acid content decreased to about 9% and α-linolenic acid to under 3%, and it does not contain any *trans*-fat (Barth, 2009). Based on the obtained results, it can be concluded that seed roasting did not significantly ($p>0.05$) affect the fatty acid composition of the examined oils. This observation is consistent with previously published results (Wijesundera *et al.*, 2008; Kraljić *et al.*, 2013).

3.5. Effect of roasting conditions on the content of tocopherols

Tocopherols are powerful lipid-soluble antioxidants that form in plants and vegetable oils. Tocopherols' ability to donate their phenolic hydrogens to lipid free-radicals is believed to play the main role in their antioxidant ability. The related antioxidant activity of the tocopherols *in vivo* is in the order of α>β>γ>δ (Kamal-Eldin and Appelqvis, 1996). Generally, a tocopherol ratio of 65% γ-tocopherol and 35% α-tocopherol is found in rapeseed oil,

TABLE 3. Fatty acid composition of rapeseed oils produced by cold pressing or pressing after roasting the seeds

Rapeseed variety	High-oleic			Yellow-seeded		
	unroasted	100 °C	150 °C	unroasted	100 °C	150 °C
Fatty acid composition	$\bar{x}$±SD	$\bar{x}$±SD	$\bar{x}$±SD	$\bar{x}$±SD	$\bar{x}$±SD	$\bar{x}$±SD
14:0	0.03±0.01^{a}	0.04±0.01^{a}	0.04±0.00^{a}	0.03±0.01^{A}	0.03±0.00^{A}	0.02±0.01^{A}
16:0	3.52±0.15^{a}	3.56±0.05^{a}	3.59±0.09^{a}	3.59±0.11^{A}	3.61±0.06^{A}	3.55±0.05^{A}
16:1	0.23±0.01^{a}	0.24±0.01^{a}	0.25±0.00^{a}	0.16±0.01^{A}	0.17±0.01^{A}	0.17±0.01^{A}
17:0	0.04±0.00^{a}	0.04±0.01^{a}	0.04±0.01^{a}	0.05±0.00^{A}	0.05±0.00^{A}	0.05±0.01^{A}
17:1	0.08±0.00^{a}	0.08±0.01^{a}	0.07±0.01^{a}	0.07±0.01^{A}	0.06±0.01^{A}	0.06±0.00^{A}
18:0	1.72±0.02^{a}	1.71±0.01^{a}	1.72±0.02^{a}	1.58±0.01^{A}	1.57±0.03^{A}	1.57±0.01^{A}
18:1	74.58±0.31^{a}	74.26±0.29^{a}	73.89±0.51^{a}	61.20±0.21^{A}	60.67±0.31^{A}	60.81±0.29^{A}
18:2	11.14±0.11^{a}	11.31±0.20^{a}	11.51±0.17^{a}	20.96±0.23^{A}	21.06±0.11^{A}	21.06±0.08^{A}
18:3	4.88±0.05^{a}	5.04±0.09^{a}	5.08±0.11^{a}	9.98±0.12^{A}	10.11±0.05^{A}	10.09±0.21^{A}
20:0	0.56±0.01^{a}	0.56±0.01^{a}	0.56±0.00^{a}	0.52±0.01^{A}	0.51±0.01^{A}	0.49±0.01^{A}
20:1	1.84±0.01^{a}	1.79±0.01^{b}	1.86±0.02^{a}	1.29±0.05^{A}	1.24±0.01^{A}	1.23±0.02^{A}
20:2	0.06±0.00^{a}	0.05±0.00^{a}	0.05±0.00^{a}	0.06±0.00^{A}	0.07±0.01^{A}	0.07±0.01^{A}
22:0	0.26±0.01^{a}	0.26±0.01^{a}	0.27±0.01^{a}	0.27±0.01^{A}	0.29±0.01^{A}	0.28±0.01^{A}
22:1	0.65±0.02^{a}	0.65±0.01^{a}	0.68±0.03^{a}	0.09±0.01^{A}	0.11±0.02^{A}	0.12±0.01^{A}
24:0	0.14±0.01^{a}	0.14±0.01^{a}	0.14±0.01^{a}	0.09±0.00^{A}	0.08±0.01^{A}	0.08±0.01^{A}
24:1	0.13±0.00^{a}	0.13±0.01^{a}	0.13±0.01^{a}	0.12±0.01^{A}	0.11±0.01^{A}	0.11±0.01^{A}
SFA	**6.36±0.13^{a}**	**6.31 ±0.05^{a}**	**6.27±0.08^{a}**	**6.13±0.09^{A}**	**6.14±0.06^{A}**	**6.04±0.06^{A}**
MUFA	**76.88±0.29^{a}**	**77.15±0.28^{a}**	**77.51±0.48^{a}**	**62.93 ±0.24^{A}**	**62.36±0.28^{A}**	**62.50 ±0.27^{A}**
PUFA	**16.08±0.16^{a}**	**16.40±0.29^{a}**	**16.64±0.28^{a}**	**31.00±0.35^{A}**	**31.24±0.16^{A}**	**31.22±0.29^{A}**
n-6/n-3	**2.28±0.00^{a}**	**2.24±0.00^{a}**	**2.7±0.02^{a}**	**2.10±0.00^{A}**	**2.08±0.00^{A}**	**2.09±0.04^{A}**

Mean values denoted by the same letter in the rows do not constitute statistically significant differences at $p<0.05$; (n=2×2).

TABLE 4. Changes in the amount of tocopherols, α-tocopherol equivalent (α-TE) and Harris coefficient of the oils produced by cold pressing or pressing after roasting seeds

Rapeseed variety		High-oleic			Yellow-seeded		
Roasting temperature [°C]		unroasted	100	150	unroasted	100	150
γ-tocopherol	[mg·100g^{-1}]	32.17^{a}	37.48^{b}	38.18^{b}	41.78^{A}	42.04^{A}	44.04^{A}
	±SD	±2.39	±2.32	±2.50	±3.63	±2.21	±2.52
	[%]	65.05	64.63	62.97	64.14	66.78	67.19
	±SD	±1.27	±1.70	±1.22	±4.80	±1.47	±1.31
α-tocopherol	[mg·100g^{-1}]	17.25^{a}	20.48^{b}	22.44^{b}	22.68^{A}	20.37^{A}	20.88^{A}
	±SD	±0.51	±0.66	±1.50	±3.29	±1.84	±2.10
	[%]	34.95	35.37	37.03	34.82	32.31	31.80
	±SD	±1.27	±1.70	±1.22	±4.86	±1.45	±1.34
Σ of tocopherols	[mg·100g^{-1}]	49.42^{a}	57.96^{b}	60.62^{b}	65.13^{A}	62.97^{A}	65.59^{A}
	±SD	±2.81	±2.30	±3.70	±2.42	±3.75	±4.51
α-TE	[mg·100g^{-1}]	20.47^{a}	24.23^{b}	26.26^{c}	26.86^{A}	24.57^{A}	25.29^{A}
	±SD	±0.71	±0.66	±1.68	±3.03	±2.0	±2.32
Harris Coefficient	–	1.23^{a}	1.48^{a}	1.63^{a}	0.87^{A}	0.79^{A}	0.81^{A}
	± SD	±0.04	±0.16	±0.05	±0.10	±0.06	±0.07

Mean values denoted by the same letter in the rows do not constitute statistically significant differences at $p<0.05$; (n=2×2).

which is consistent with the results obtained in this study. The largest amounts of γ-tocopherol were detected, followed by α-tocopherol, but the amount of individual tocopherols varied significantly, depending primarily on the rapeseed variety (Table 4). In this study, no β-tocopherols were

detected or their amounts were below the limits of sample quantification. In cold-pressed oil samples, both γ-and α-tocopherol concentrations were higher in the oil obtained from yellow-seeded *B. napus* than in the oil from high-oleic rapeseed (41.7 vs. 32.17 mg·100 g^{-1} of γ-tocopherol and 22.68 vs. 17.25 mg·100 g^{-1} of α-tocopherol, respectively). There were also noticeable differences in individual tocopherol contents depending on the applied roasting temperature. By comparing the data given in Table 4, it can be seen that a slight increase in the γ-tocopherol concentration occurred with a higher roasting temperature, while there was no explicit influence of roasting conditions on the amount of α-tocopherol. Vaidya and Choe (2011) suggested that the increased release of tocopherols, and their increased amount in extracted oil, is a result of heat-induced oilseed cell damage. Wijesundera *et al.* (2008) reported that conditioning rapeseed at the temperature of 165 °C resulted in a modest increase in γ-tocopherol concentration with a practically unchanged content of α-tocopherol. However, Kraljić *et al.* (2013) found that a moderate rapeseed conditioning temperature (80 °C) increased the α-tocopherol content, but no significant difference in the amount of γ-tocopherol was observed. On the other hand, Prior *et al.* (1991a) found that roasting rapeseed (*B. napus* cv. *Westar*) at 80 °C slightly decreased its α-tocopherol content, whereas roasting the seeds at 100 °C resulted in an increase in the amount of α-tocopherol (17.3 vs. 21.0 mg/100 g). Along with roasting temperature elevation, a statistically significant (p<0.05) increase in vitamin E concentration (expressed as α-TE) occurred in the oil samples produced from the high-oleic rapeseed variety, while no such relationship was observed for oil pressed from the yellow-seeded rapeseed variety (Table 4). In order to determine changes in the nutritional value of the examined oils, the Harris coefficient was calculated. Along with elevated roasting temperature, an increase in the Harris coefficient was observed due to the increased extractability of tocopherols from the seeds. Aside from roasting conditions, oils obtained from high-oleic rapeseed were characterized by a higher Harris coefficient, ranging from 1.23 to 1.63. The calculated Harris coefficient for the oils obtained from yellow-seeded rapeseed was nearly twice as low, but it also maintained its proper physiological value (α-TE to PUFA ratio (mg/g) of 0.6:1, as a minimum to protect against PUFA peroxidation) (Eitenmiller and Lee, 2004).

3.6. Effect of roasting conditions on the content of pigments

Carotenoid and chlorophyll pigments represent the natural components of oilseeds, which are partially extracted into crude oils during industrial oilseed processing using pressing or extraction. Pigments are considered important factors as they can impart undesirable color to vegetable oils or facilitate oxidation in the presence of light (Endo *et al.*, 1992). The concentration of carotenoid pigments (λ=445) was nearly twice as high in oils pressed using rapeseed subjected to roasting than using untreated samples (Figure 2). Increased carotenoid content in the oils extracted from seeds subjected to thermal

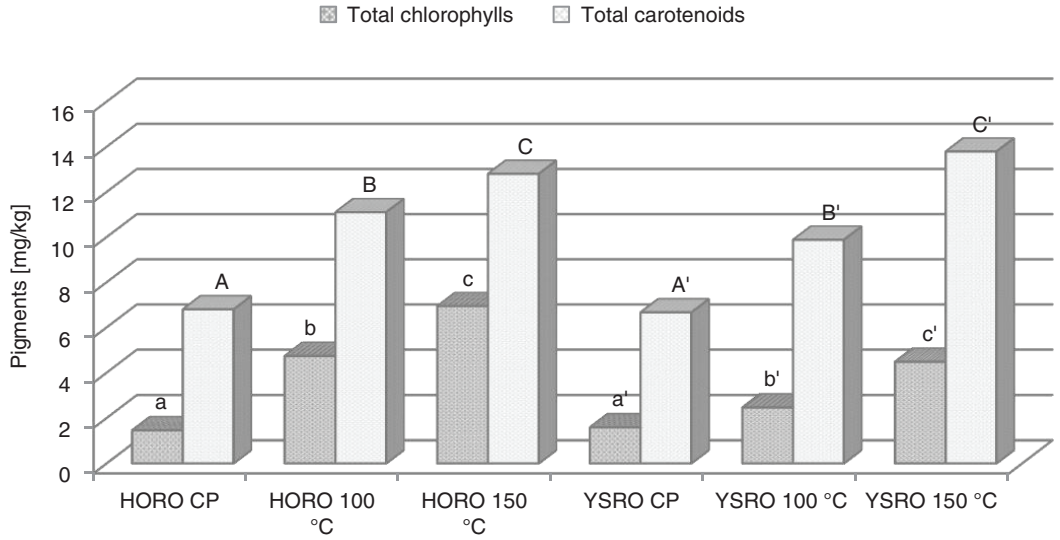

FIGURE 2. Pigments (mg·kg^{-1}) in rapeseed oils produced by cold pressing or pressing after roasting seeds.
Explanatory notes: HORO–high-oleic rapeseed oil; YSRO–yellow-seeded rapeseed oil;
100, 150 °C–roasting temperature; CP–cold-pressed.
Mean values denoted by different letters in columns constitute statistically significant differences at p<0.05; (n=2×2).

pre-treatment could be partially explained by the fact that carotenoids bind to proteins inside the seed during heat treatment and form thermo-stable carotenoid-protein complexes. A thermal-induced process of protein denaturation and destruction of the internal seed cell structure increases the oil's accessibility to lipid-soluble carotenoids (Vaidya and Choe, 2011). Additionally, during thermal treatment, chlorophylls are converted into pheophytins (mainly *a* and *b*) and pheophorbide (Endo *et al*., 1992). Within each rapeseed variety, along with increasing roasting temperature, a statistically significant ($p<0.05$) increase in the content of pheophytin *a* was observed (Figure 2). Pheophytin *a* content was from twice to nearly 4 times higher in the oils obtained from seeds subjected to roasting prior to pressing compared to cold-pressed oils. Similar findings were published by Górecka *et al*. (2003), and Kraljić *et al*. (2013), who found that conditioning rapeseed prior to pressing has a significant impact on an increased abundance of pigments in oil.

3.7. Effect of roasting conditions on the oil stability

The oxidative stability of vegetable oils is influenced by many factors, especially the fatty acid composition, antioxidants, mainly tocopherols and minor compounds (Kamal-Eldin, 2006). As shown in Table 2, the IPs of the tested oils indicated a variety-dependent range of oxidative stabilities with superior oxidative stability in high-oleic *B. napus* compared to yellow-seeded *B. napus*. Roasting the seeds prior to pressing improved the oxidative stability of the oil obtained from both rapeseed varieties; however, a statistically significant increase in oxidative stability was achieved by roasting the seeds at 150 °C. The IP length differences of the examined oils can be partially explained by the FA composition. Yellow-seeded rapeseed exhibits a typical fatty acid composition of a 00-rapeseed. Thus, an increase in oxidative stability is comparable to the results obtained in the studies employing different 00-rapeseed varieties as a research material, which is subjected to roasting prior to pressing (Prior *et al*., 1991b; Górecka *et al*., 2003; Wijesundera *et al*., 2008). An increased oleic acid content and decreased α-linolenic acid content in high-oleic rapeseed oil is believed to play the main role in increasing the oxidative stability of oils (Merrill *et al*., 2008). The effects of roasting conditions on the oxidative stability of the oil obtained from high-oleic rapeseed have not yet been investigated. The oxidative stability of the high-oleic/low-linolenic rapeseed oil in studies conducted by Matthäus (2006) was 7.3 h, exceeding the oxidative stability of the cold-pressed high-oleic rapeseed oil obtained in this study (6.88 h), but approaching that of the oil from 100 and 150 °C-roasted seeds (7.24 and 7.62, respectively).

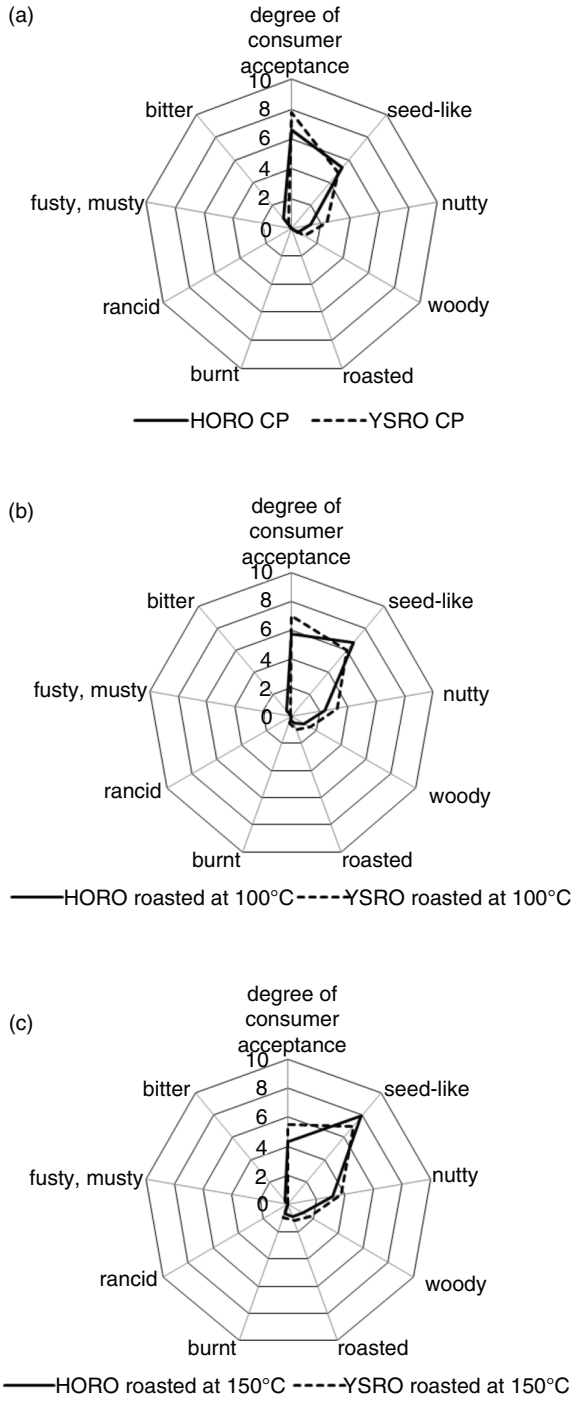

FIGURE 3. Sensory profiles of cold-pressed (A) and *virgin* rapeseed oils (B, C). Explanatory notes: HORO–high-oleic rapeseed oil; YSRO–yellow-seeded rapeseed oil; 100, 150 °C–roasting temperature; CP–cold-pressed.

3.8. Sensory assessment of oils

Figure 3 illustrates the sensory evaluation results for cold-pressed and *virgin* rapeseed oils. Along with increased roasting temperature, an explicit increase in

"seed-like" and "nutty" aroma descriptors (which are construed as positive attributes for perceived sensations) was observed (Figure 3 B, C). Moreover, the "roasted" attribute appeared in the oils obtained from seeds subjected to thermal treatment prior to pressing. This attribute is a characteristic flavor descriptor for *virgin* rapeseed oils produced with heat-treatment during processing (Brühl and Matthäus, 2008). Seed roasting conducted at 150 °C resulted in the most noticeable "roasted" aroma (1.2 and 0.9 for yellow-seeded and high-oleic rapeseed oil, respectively) (Figure 3 C). Furthermore, a "burnt" aroma was detectable in oil samples obtained from seeds heated at 150 °C (1.0 and 0.7 for oil obtained from yellow-seeded and high-oleic rapeseed, respectively). On the other hand, oils obtained from thermally pretreated seeds were less acceptable from the sensory point of view in comparison to cold-pressed oils. The most noticeable decrease in consumer acceptance was observed in the oils obtained from seeds roasted at 150 °C (5.5 and 4.3 for yellow-seeded and high-oleic rapeseed oil, respectively), most likely due to the appearance of a "burnt" off-flavor.

4. CONCLUSIONS

The results indicate that roasting rapeseed prior to pressing did not alter the fatty acid composition of the oil, which is relevant from the nutritional point of view. However, high-oleic rapeseed oil exhibited a nearly 2-fold increase in oxidative stability compared to the oil obtained from yellow-seeded rapeseed, which can be partially explained by the differences in the fatty acid composition of the examined oils. Furthermore, seed roasting increased the amount of γ-tocopherol, which can be attributed to the prolongation of the oil's oxidative stability. Nevertheless, an increased degree of hydrolysis and oxidation of lipids, assessed in terms of changes in characteristic values, was reported; however, the obtained results were within Codex Alimentarius limits. Roasting conducted at the temperature of 150 °C resulted in the highest oil yield and the highest extractability of pigments; however, sensory assessment revealed that rapeseed oils obtained from 100 °C-roasted seeds met with greater consumer acceptance.

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