

Article

Improvement of Refined Rapeseed Oil Thermal Resistance by Native Antioxidants Present in Rapeseed, Coriander, and Apricot Cold-Pressed Oils

Monika Fedko ^{1,*}, Aleksander Siger ² and Dominik Kmiecik ^{3,*}¹ Warsaw University of Life Sciences–SGGW, 166 Nowoursynowska Street, 02-787 Warsaw, Poland² Department of Food Biochemistry and Analysis, Poznań University of Life Sciences, Wojska Polskiego 31, 60-634 Poznań, Poland; aleksander.siger@up.poznan.pl³ Department of Food Technology of Plant Origin, Poznań University of Life Sciences, Wojska Polskiego 31, 60-634 Poznań, Poland

* Correspondence: monika_fedko@sggw.edu.pl (M.F.); dominik.kmiecik@up.poznan.pl (D.K.)

Abstract

The research aimed to evaluate the effect of high monounsaturated cold-pressed oil addition on the inhibition of refined rapeseed oil degradation during heating at frying temperature. Cold-pressed rapeseed, coriander seed, and apricot kernel oils were added in amounts of 5 and 25%. Refined rapeseed oil without additives and refined rapeseed oil supplemented with tert-butylhydroquinone (TBHQ) were negative and positive control samples, respectively. Blends were heated in a thin layer at 170 and 200 °C. Considering the increase in total polar compounds (TPCs) and oxidized triacylglycerol monomer (oxTAG) content, natural additives demonstrated protective properties and were more effective than the TBHQ additive, especially at 200 °C. The lowest increases in TPC and oxTAG were found in AO5% at 170 °C (10.17% and 1.40 mg/g oil, respectively) and in AO25% at 200 °C (5.71% and 47.53 mg/g oil, respectively). The presence of triacylglycerol (TAG) dimers was found only in samples heated at 200 °C, and the lowest was in the sample with 25% coriander oil. It can be concluded that the addition of cold-pressed oils limited the TAG oxidation process. The addition of 25% coriander oil was effective in inhibiting the TAG polymerization process, and it may be a powerful alternative to synthetic antioxidants in improving stabilization of frying oils.

Keywords: total polar compounds; polymers of triacylglycerols; frying; thermal stability of oil; antioxidant activity; tocopherols; cold-pressed oils

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1. Introduction

Vegetable oils are a rich source of bioactive substances such as tocochromanols and phytosterols [1–4], which may limit triacylglycerol (TAG) degradation during frying [5–7]. However, these substances are characterized by varied, often high lability under high temperature conditions used during thermal treatment [8,9]. Oils obtained from different raw materials differ in their stability under high temperature conditions depending on the fatty acid composition and bioactive substance content and composition [1–4]. In turn, the properties of individual types of bioactive substances depend mainly on their structure but also on the environmental factors, the occurrence of synergistic or antagonistic interactions, and other interactions with the matrix [10–12].

Frying is a common and easy method of preparing delicious food products, including meatballs, pancakes, and fried potatoes. Fried foods are appreciated by consumers for their unique taste, smell, golden color, and crunchiness. However, the high temperature of frying induces various chemical reactions in oils, mainly the degradation of TAG, such as oxidation, hydrolysis, polymerization, isomerization, and cyclization. It leads to the generation of undesirable, hazardous substances in the oil, including oxidized TAG monomers (oxTAGs), TAG polymers, epoxy fatty acids, volatile aldehydes, and cyclic fatty acids [13–16]. This may depend on many factors, including the type of oil used, the frying temperature, and the duration of the frying process [17–20]. Oil degradation products are transported into the food along with the oil. Lipid oxidation products may induce oxidative stress, leading to damage to DNA and cell membranes as well as activation of inflammatory pathways [21–23]. Consumption of food with a high level of oil degradation products may lead to the development of cancer, diabetes, obesity, coronary artery disease [24], Parkinson's disease, Alzheimer's disease, as well as anxiety and depression due to neuroinflammation [25] and other serious medical conditions [26]. Considering the above points, preventing oil degradation has become a highly relevant, significant, and pressing concern.

Synthetic antioxidants like tert-butylhydroquinone (TBHQ) may be used to delay the formation of degradative products during frying [27,28]. However, they are suspected to exhibit a negative impact on health [29–31]. This has led to growing interest in natural antioxidants, like the extracts of herbs, fruits, and seed cake [32–34]. Usually, natural extracts are based on polar solvents like ethanol, methanol, or water, and therefore, they have low solubility in oil, which hinders their practical application. An alternative approach could involve the use of nanoemulsion, encapsulated natural antioxidants, and complexing agents such as cyclodextrin, which trap bioactive compounds [35,36]. However, this is a technologically complicated method that is difficult to use on an industrial scale, requiring expensive, advanced equipment, and therefore, its practical application remains challenged. Cold-pressed oils are lipophilic substances that can be easily mixed with frying oils like refined rapeseed oil. They are sources of antioxidants, bioactive substances including tocochromanols, phytosterols, and phenolic compounds [37–41], which may show protective properties during oil heat treatment. Therefore blends of cold-pressed oils may exhibit better thermal stability than oils typically used for frying [42,43]. Interesting results were reported by Ramroudi et al. [44], who found that corn–sesame oil and sunflower–sesame oil blends had higher oxidative stability than base oils. This effect may be attributed to the synergistic activity of natural antioxidants in oils. However, an important issue is that inappropriate storage conditions of oil, including elevated ambient temperature, exposure to light, and access to oxygen, may induce and accelerate oil oxidation [45]. One of the main limitations in the practical application of oil blends is that their stability, properties, and benefits depend strongly on the oil composition, including fatty acid profile and antioxidant concentration, and therefore it requires comprehensive research.

It should be noted that blending oils with different fatty acid profiles may also affect the oxidative stability and nutritional properties of the resulting blends. Many cold-pressed oils are characterized by a high proportion of polyunsaturated fatty acids, which makes them more susceptible to oxidative processes [41,46,47]. On the other hand, it is commonly known that high saturated fatty acid (SFA) consumption is related to an increased risk of coronary heart disease [48,49]. Therefore, incorporating cold-pressed oils rich in monounsaturated fatty acids (MUFAs) allows the appropriate balance to be maintained in terms of the level of unsaturation and appears to be the most rational approach in frying applications.

However, the effect of the fatty acid profile in individual foods on human health is a more complex issue. It depends on various factors, including the ratio between individual fatty acids and their effect on the functions of the cardiovascular and immune systems. Therefore, several indicators are used to facilitate the evaluation and comparison of lipid nutritional quality among different foods. The proper proportion between n-6 and n-3 is important for maintaining homeostatic balance in the body. Excessive consumption of n-6 and insufficient n-3 can lead to a number of health problems, including inflammation, cancer, obesity, diabetes, and neurodegenerative diseases [50–52]. According to various sources, the n-6/n-3 ratio in a healthy, balanced diet ranges from 10:1 to 2:1, or even ~1 [50,53]. In contrast, the typical diet in industrialized, Western countries differs markedly from these guidelines, showing an n-6/n-3 ratio of about 20:1, while in South Asia the ratio may reach 50:1 [54]. A PUFA/SFA ratio above 0.45 is recommended by the British Department of Health [55] to reduce the adverse effects of elevated LDL levels. However, this index does not consider MUFAs, which have an important role in lipid balance. Santos-Silva et al. [56] proposed the use of a hypocholesterolemic/hypercholesterolemic (HH) ratio, a high value of which indicates a favorable effect on cholesterol metabolism. The atherogenicity index (AI) expresses the tendency for plaque accumulation and elevated cholesterol level in blood. In turn the thrombogenicity index (TI) reflects the potential for clot formation in blood vessels. Therefore, foods with low AI and TI values are desirable for minimizing coronary artery disease risk [57], and it is assumed that both should be below 1 [58]. High consumption of myristic and palmitic acids is considered to contribute to atherogenic and thrombogenic effects. However, lauric acid is associated with an atherogenic effect but does not affect thrombogenicity. Similarly, stearic acid exhibits pro-thrombogenic activity but is believed to be neutral regarding atherogenicity [59]. On the other hand, MUFAs and PUFAs are both associated with anti-atherogenic and anti-thrombogenic properties [60].

The aim of the study was to evaluate the possibility of limiting oxidation and TAG polymerization processes in refined rapeseed oil by adding highly monounsaturated cold-pressed oils, including rapeseed, coriander, and apricot oils, during heating at frying temperature.

2. Materials and Methods

2.1. Research Material

Refined rapeseed oil (Kujawski, Bunge Polska Sp. z o. o., Kruszwica, Poland) was purchased at a local grocery store. Cold-pressed rapeseed oils (Olini, Świebodzice, Poland), cold-pressed coriander seed oil (Efavit, Poznań, Poland), and cold-pressed apricot kernel oil (Olini, Świebodzice, Poland) were obtained directly from the local cold-pressed oil producers. Cold-pressed rapeseed oils, cold-pressed coriander seed oil, and cold-pressed apricot kernel oil were designated as RO, CO, and AO, respectively.

2.2. Blends Preparation

Refined rapeseed oil without additives (RefO) and refined rapeseed oil with the addition of 200 mg TBHQ/kg oil (rTBHQ) were negative and positive control samples, respectively. Six types of blends were prepared by blending refined rapeseed oil with cold-pressed rapeseed oil (RO5% and RO25%), cold-pressed coriander seed oil (CO5% and CO25%), and cold-pressed apricot kernel oil (AO5% and AO25%), each at a concentration of 5 and 25% (v/v). Blends were prepared in the dark glass bottles. Next, the bottles were sealed in a nitrogen atmosphere and mixed for 1 h at room temperature using an IKA KS 501 shaker (IKA Poland Sp. z o.o., Warszawa, Poland). Samples were left for 24 h in the dark at 4 °C before further procedures.

2.3. Heating Procedure

Each sample of blends and refined rapeseed oil was heated at two temperatures, 170 and 200 ± 10 °C. Heating was performed using MS-H-Pro (Scilogex, Rocky Hill, CT, USA) hotplates equipped with external temperature control in a fume hood with an air flow of 6 m³/min. A total of 50 mL of oil was heated in a thin layer, exposed to air, on a flat pan with a diameter of 20 cm in two repetitions for both temperatures. The ratio of surface area to air to oil volume was 6.30 cm⁻¹. In the first stage, oils were heated for 7 min to reach 170 ± 10 °C or 9 min to 200 ± 10 °C. In the second stage, oils were heated for 10 min, maintaining a temperature of 170 ± 10 °C or 200 ± 10 °C. The actual oil temperature was continuously monitored using an electronic Testo mini surface thermometer (Testo SE & Co KGaA, Titisee-Neustadt, Germany) at three points on the pan. After cooling down, the oil samples were transferred to plastic containers, sealed in a nitrogen atmosphere, and stored in darkness at a temperature −30 °C until the analysis.

2.4. Fatty Acid Groups

Based on the fatty acid composition data from our previous research [61], the share of saturated (SFAs), monounsaturated (MUFAs), and polyunsaturated (PUFAs) fatty acids was calculated according to the following formulas:

$$SFA = C14:0 + C16:0 + C18:0 + C20:0 + C22:0, \quad (1)$$

$$MUFA = C16:1 + C18:1 + C20:1, \quad (2)$$

$$PUFA = C18:2 + C18:3, \quad (3)$$

2.5. Calculation of Iodine Value

Based on the fatty acid composition data from our previous research [61], the iodine value was determined according to the AOCS Official Method [62].

2.6. Indices of Lipid Nutritional Quality

The composition lipid nutritional quality indices were calculated using the fatty acid composition data from our previous research [61] according to formulas from Kmiecik et al. [63]. The PUFA/SFA ratio refers to balance between the polyunsaturated fatty acid sum and saturated fatty acid sum. The index of atherogenicity (IA), index of thrombogenicity (IT), and hypocholesterolemic/hypercholesterolemic (HH) ratio were determined as follows:

Index of Atherogenicity

$$IA = \frac{C12:0 + (4 \times C14:0) + C16:0}{\Sigma MUFA + \Sigma PUFA} \quad (4)$$

Index of Thrombogenicity

$$HH = \frac{C14:0 + C16:0 + C18:0}{0.5 \times \Sigma MUFA + 0.5 \times \Sigma n - 6 PUFA + 3 \times \Sigma n - 3 PUFA + \frac{\Sigma n - 3 PUFA}{\Sigma n - 6 PUFA}} \quad (5)$$

Hypocholesterolemic/Hypercholesterolemic (HH) Ratio

$$HH = \frac{C18:1 + \Sigma PUFA}{C12:0 + C14:0 + C16:0} \quad (6)$$

2.7. Color Index Analysis

The color of the oils was determined according to the AOCS Official Method [64]. The oil sample (1 g) was dissolved in 2 mL of isooctane (≥99.5%, Chempur, Piekary Śląskie,

Poland) and mixed on a vortex. The color was measured with a spectrophotometer at 490 nm. Isooctane was used as the blank.

2.8. Total Polar Compound Content Analysis

The content of total polar compounds (TPCs) in the oils was analyzed according to AOCS Official Method [65]. Firstly, the oil sample was weighed, dissolved in toluene ($\geq 99.9\%$, Merck, Darmstadt, Germany), and introduced on top of silica gel columns. The nonpolar fraction was eluted with a mixture of hexane ($\geq 99\%$, Merck) and diisopropyl ether ($\geq 99\%$, Merck) (82:18, *v/v*), collected, and weighed after solvent removal. Next, the polar fraction was calculated based on the weight difference of the sample and the nonpolar fraction. The results were expressed as a percentage of the total content of the oil sample. The increase in TPC content after heating at 170 °C was calculated as the difference between the mean TPC content in the oil after heating at 170 °C and the mean TPC content in the unheated oil. The increase in TPC content after heating at 200 °C was calculated as the difference between the mean TPC content in the oil after heating at 200 °C and the mean TPC content in the unheated oil.

2.9. Oxidized TAG Monomer Content and TAG Polymer Content Analysis

Oxidized TAG monomer (oxTAG) content and TAG polymer content were determined according to Kmiecik et al. [66] in the polar fraction, which was eluted from silica gel columns after the nonpolar fraction. This process was carried out by high-performance size-exclusion chromatography (HPSEC) with an injection sample volume of 1 mL, column temperature of 30 °C, and detector temperature of 30 °C. Dichloromethane ($\geq 99\%$, Merck) was the liquid phase with a flow rate of 1 mL/min. Analysis was performed using an Infinity 1290 HPLC system (Agilent Technologies, Santa Clara, CA, USA) coupled with an ELSD (Evaporative Light Scattering Detector) and two connected Phenogel columns (100 Å and 500 Å, 5 µ, 300 × 7.8 mm) (Phenomenex, Torrance, CA, USA). The increase in oxTAG content after heating at 170 °C was calculated as the difference between the mean oxTAG content in the oil after heating at 170 °C and the mean oxTAG content in the unheated oil. The increase in oxTAG content after heating at 200 °C was calculated as the difference between the mean oxTAG content in the oil after heating at 200 °C and the mean oxTAG content in the unheated oil.

2.10. Statistical Calculation

Frying oil processes were carried out in duplicate, and all analyses were performed in duplicate. The results for samples of unheated blends and cold-pressed oils are the average of two determinations $\pm$ standard deviation (SD). The results for heated samples are expressed as the means of four determinations $\pm$ standard deviation (SD). One-way analysis of variance (ANOVA) with Tukey's multiple range tests ($p < 0.05$) and Pearson's correlation analysis was conducted with Statistica 13.3 software. Moreover, the data were standardized and subjected to principal component analysis (PCA) by Statistica 13.3 software. Charts were prepared in Statistica 13.3 and MS Excel 2019.

3. Results and Discussion

3.1. Characteristics of Cold-Pressed Oils

MUFAs were the predominant fatty acids in cold-pressed oils and ranged from 82.92% (CO) to 66.81% (RO) (Table 1). The second-most abundant group in RO and AO was PUFAs, which constituted 25.86% in RO and 23.40% in AP. The share of PUFAs and SFAs in CO was comparable, amounting to 8.17% and 8.89%, respectively. The SFA share was the highest in CO but only 2.35% and 3.26% higher than in RO and AO, respectively.

The calculated iodine value (CIV) ranked in the following descending order: 110.91 (RO), 101.67 (AO), and 85.73 (CO). The PUFA/SFA ratio ranged from 4.16 (AO) to 0.92 (CO). The n-6/n-3 ratio ranged from 1.83 (RO) to 355.73 (AO). CO exhibited the highest AI and TI values and the lowest hypocholesterolemic/hypercholesterolemic ratio. The total polar compounds (TPCs) and oxidized TAG monomers (oxTAGs) varied between 4.10 and 6.07% and between 40.29 and 56.77 mg/g oil, respectively.

Table 1. Physicochemical parameters of cold-pressed oils.

	RO	CO	AO
SFAs [%]	6.54 ± 0.04 a	8.89 ± 0.04 b	5.63 ± 0.01 c
MUFAs [%]	66.81 ± 0.04 a	82.92 ± 0.07 b	70.96 ± 0.01 c
PUFAs [%]	25.86 ± 0.02 a	8.17 ± 0.04 b	23.40 ± 0.02 c
CIV [g I/100 g of oil]	110.91 ± 0.01 a	85.73 ± 0.00 b	101.67 ± 0.02 c
PUFA/SFA	3.96 ± 0.02 a	0.92 ± 0.00 b	4.16 ± 0.01 c
n-6/n-3	1.83 ± 0.00 a	23.82 ± 0.64 b	355.73 ± 10.27 c
HH	22.16 ± 0.08 a	18.97 ± 0.00 b	21.05 ± 0.05 c
AI	0.046 ± 0.000 a	0.054 ± 0.000 b	0.048 ± 0.000 c
TI	0.084 ± 0.000 a	0.172 ± 0.001 b	0.116 ± 0.000 c
color index	0.056 ± 0.002 a	1.088 ± 0.002 b	0.136 ± 0.001 c
total polar compounds [%]	4.10 ± 1.07 a	6.07 ± 0.62 a	5.80 ± 0.49 a
oxidized TAG monomers [mg/g oil]	40.29 ± 10.78 a	56.77 ± 5.71 a	56.47 ± 5.00 a

RO—cold-pressed rapeseed oil; CO—cold-pressed coriander seed oil; AO—cold-pressed apricot kernel oil. The values are the means of two determinations ± SDs. SFAs—saturated fatty acids; MUFAs—monounsaturated fatty acids; PUFA/SFA—polyunsaturated and saturated fatty acid ratio; CIV—calculated iodine value; HH—hypocholesterolemic/hypercholesterolemic ratio; AI—atherogenicity index; TI—thrombogenicity index. Means in the same row followed by different letters indicate significant differences ($p < 0.05$) between samples.

3.2. Fatty Acid Groups and Calculated Iodine Value (CIV)

In unheated blends, MUFAs had the predominant share, with the highest value observed in CO25% (70.16%) and the lowest in rTBHQ (65.72%) (Figure 1). PUFAs were second among fatty acid groups and ranged from 22.76% (CO25%) to 27.78% (RefO). CO25% had the highest SFA share (6.93%), while AO25% had the lowest (5.91%). Concerning the CIV, it varied between 105.89 and 112.82, and it followed the PUFA share. The most pronounced effect of additives on the fatty acid group composition was observed in blends containing coriander oil, CO5% and CO25%, in which the MUFA share increased by 2.29% and 4.43%, respectively, and the PUFA share decreased by 2.40% and 5.01%, respectively. However, the change in the SFA share was minor and varied from 0.05% to 0.62%. Detailed data on fatty acid group CIVs are presented in Table S1 (Supplementary Materials).

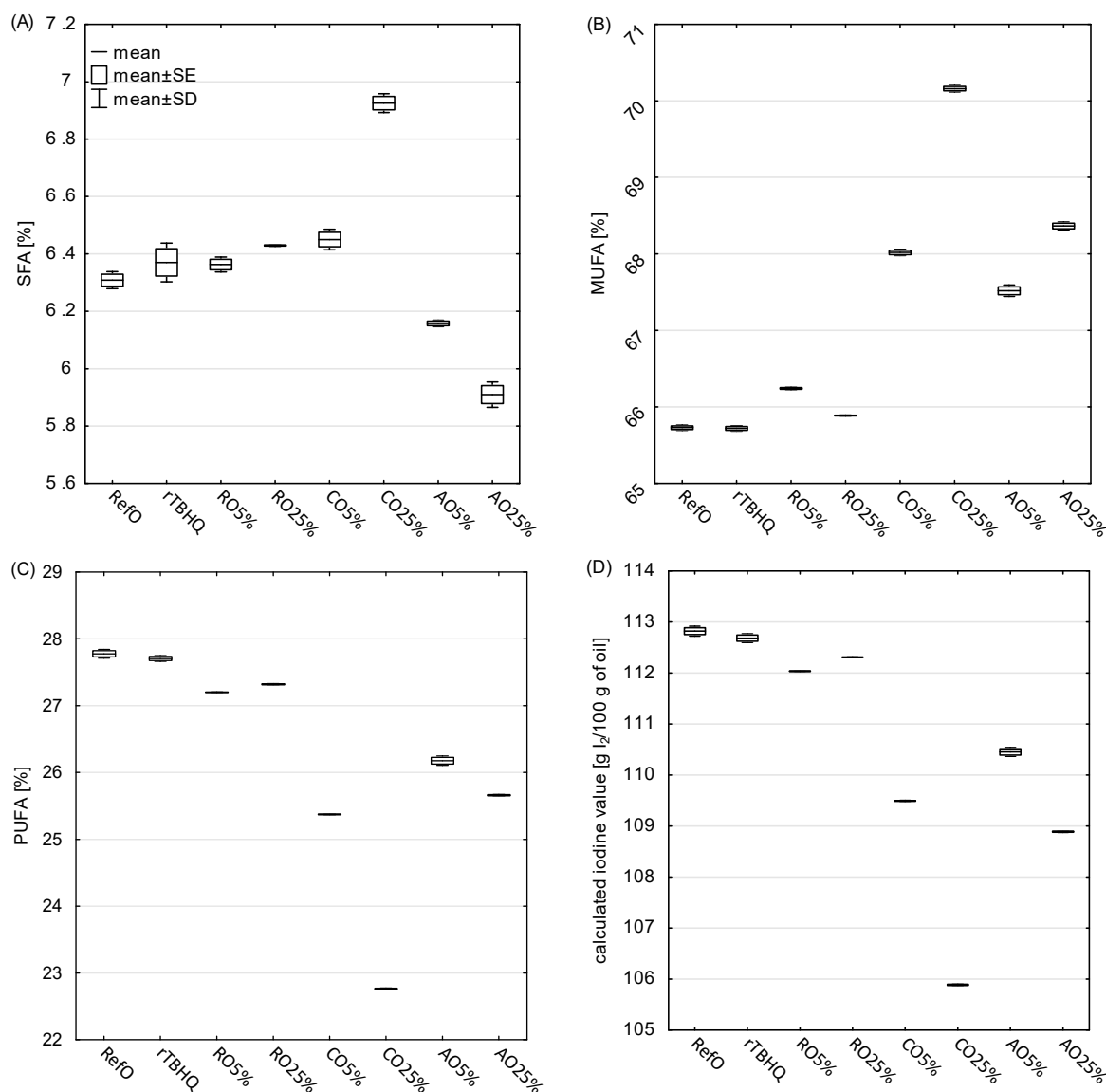


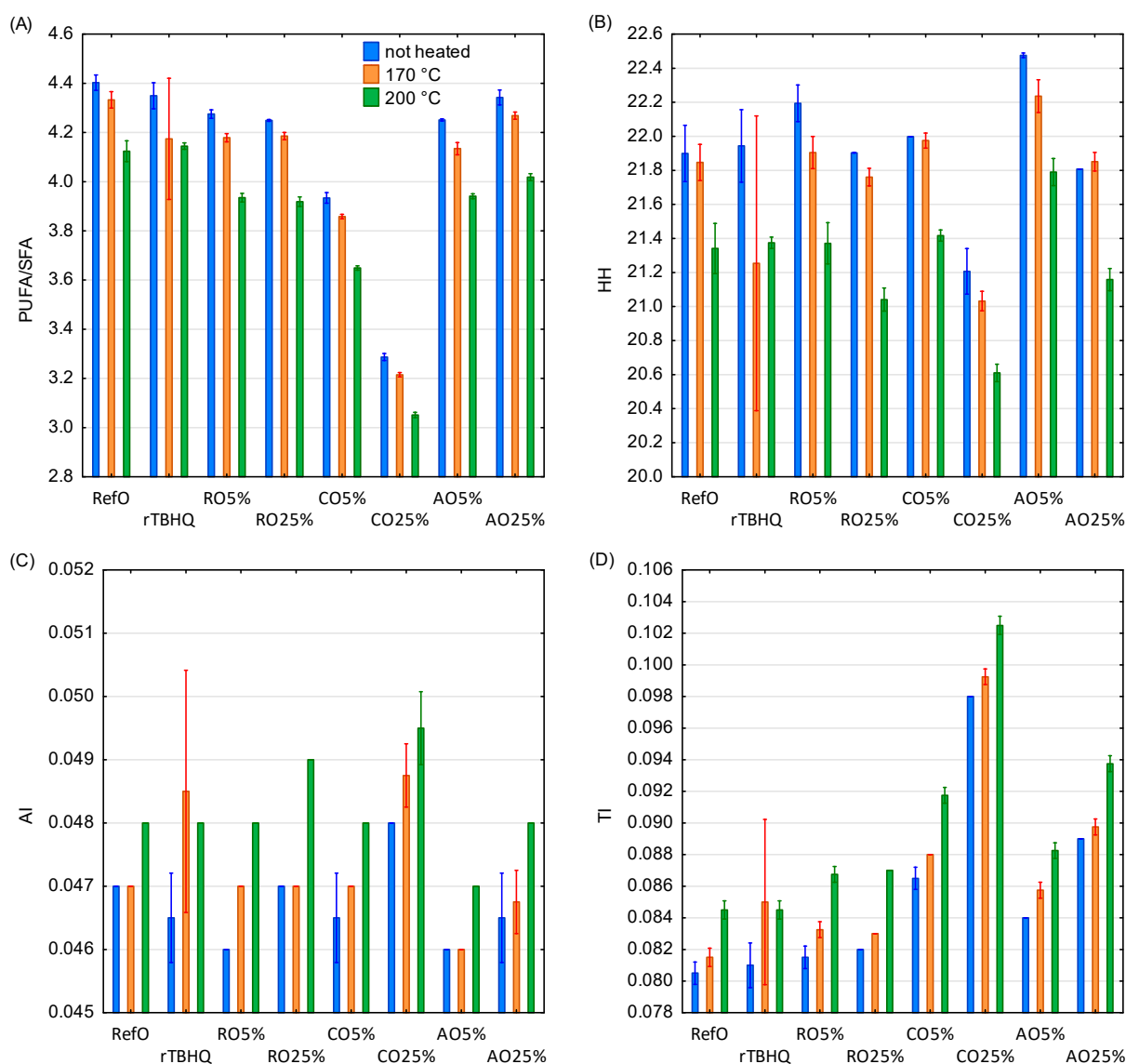
Figure 1. The shares of main fatty acid groups (A) saturated fatty acid (SFA); (B) monounsaturated fatty acid (MUFA); (C) polyunsaturated fatty acid (PUFA) and (D) calculated iodine value in oil blends. RefO—refined rapeseed oil; rTBHQ—refined rapeseed oil with the addition of tert-butylhydroquinone; RO5%—a blend of refined rapeseed oil and 5% cold-pressed rapeseed oil; RO25%—a blend of refined rapeseed oil and 25% cold-pressed rapeseed oil; CO5%—a blend of refined rapeseed oil and 5% cold-pressed coriander seed oil; CO25%—a blend of refined rapeseed oil and 25% cold-pressed coriander seed oil; AO5%—a blend of refined rapeseed oil and 5% cold-pressed apricot kernel oil; AO25%—a blend of refined rapeseed oil and 25% cold-pressed apricot kernel oil. SD—standard deviation; SE—standard error.

3.3. Indices of Lipid Nutritional Quality

In unheated blends and control samples, the ranges of AI and TI values were narrow, ranging from 0.046 to 0.048 and from 0.081 to 0.098, respectively (Figure 2). However, PUFA/SFA and HH values showed greater variability. PUFA/SFA and HH had the lowest CO25% (3.29 and 21.21, respectively). RefO had the highest PUFA/SFA (4.40), and the AO5% blend was characterized by the highest HH ratio (22.48). Among tested additives, coriander oil had the greatest effect on the change in dietary indices. In CO25%, the TI value increased by 21.00% relative to RefO, whereas PUFA/SFA and HH values decreased by 25.35% and 3.16%, respectively. Among the blends, CO25% had the most atherogenic, thrombogenic, and hypercholesterolemic composition, resulting from an increase in the

SFA share and a decline in the PUFA share, despite an increase in the MUFA share. However, in all samples AI, TI, and PUFA/SFA values were within globally accepted recommendations [55,58]. In CO25% AI and TI values were more than 20- and 10-fold lower than the maximum recommended value, respectively, and the PUFA/SFA level was more than 7-fold higher than the minimum recommended value. According to our knowledge, no specific recommendation exists for the HH ratio, but higher values are beneficial for maintaining a favorable blood lipid profile. Compared to the Cornicabra olive oil variety (6.61) [63], the white açai oil variety (3.344) [67], and avocado oil (2.79) [68], the HH ratios for CO25% were more than 3-, 4-, and 7-fold lower, respectively.

In unheated samples, the lowest n-6/n-3 ratio was observed in RO25% (2.00), and it was 1/3 of the highest n-6/n-3 ratio in AO25% (3.06). Generally, all samples were close to each other. However, three groups could be distinguished. The first group, with an n-6/n-3 ratio between 2.00 and 2.05, included control samples (RefO and rTBHQ) and blends with cold-pressed rapeseed oil (RO5% and RO25%). The second group, with an n-6/n-3 ratio between 2.24 and 2.35, comprised blends of coriander oil (CO5% and CO25%) and one of blends of apricot oil (AO5%). In the last group there was only one blend with 25% apricot oil (AO25%), which was the most different from the others. It is worth noting that in all blends, the n-6/n-3 ratio was below the value indicated by the WHO and FAO [53].



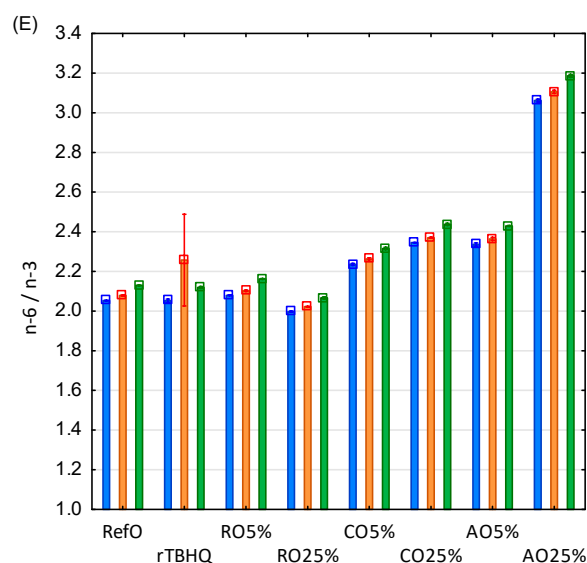


Figure 2. The changes in (A) polyunsaturated and saturated fatty acid ratio (PUFA/SFA); (B) hypocholesterolemic/hypercholesterolemic ratio (HH); (C) atherogenicity index (AI); (D) thrombogenicity index (TI) (E) n-6 fatty acids to n-3 fatty acid ratio (n-6/n-3) in blends unheated and heated at 170 and 200 °C. RefO—refined rapeseed oil; rTBHQ—refined rapeseed oil with the addition of tert-butylhydroquinone; RO5%—a blend of refined rapeseed oil and 5% cold-pressed rapeseed oil; RO25%—a blend of refined rapeseed oil and 25% cold-pressed rapeseed oil; CO5%—a blend of refined rapeseed oil and 5% cold-pressed coriander seed oil; CO25%—a blend of refined rapeseed oil and 25% cold-pressed coriander seed oil; AO5%—a blend of refined rapeseed oil and 5% cold-pressed apricot kernel oil; AO25%—a blend of refined rapeseed oil and 25% cold-pressed apricot kernel oil.

With regard to heated blends, PUFA/SFA levels decreased at both temperatures, and the decrease was between 2.7- and 5.1-fold higher at 200 °C than at 170 °C. Similarly, an HH ratio drop was observed at both temperatures. Heating at 170 °C did not cause changes in AI except for rTBHQ, RO5%, and CO25%. At 200 °C a slight increase in AI was observed in all blends. Insight into TI showed a slight rise at both temperatures; at 200 °C it was 4- or 5-fold higher than at 170 °C. The TI value was the same at 170 and 200 °C only in rTBHQ. The results from this study are consistent with previous surveys [63,69], which showed that heating and frying caused a MUFA and PUFA decrease as well as an SFA increase, which lead to intense atherogenic, thrombogenic, and hypercholesterolemic effects. In all samples an increase in the n-6/n-3 ratio was noted after heating at both temperatures, but it had reached maximum by 0.2 and ranged from 6.28 to 10.01% of initial value. This was probably due to the greater susceptibility to degradation of α -linolenic acid than linoleic acid. Detailed data on lipid nutritional quality indices are presented in Table S2 (Supplementary Materials).

3.4. Color Index

Color serves as a rapid indicator for assessing frying oil quality. As can be seen in Figure 3, among unheated samples, the highest color index was observed in RO25% (0.267), and it results from natural chlorophyll content in cold-pressed rapeseed oil, as reported in our previous study [61] for this bioactive compound amount in the same samples. In other blends, values were similar, ranging from 0.012 to 0.066. As expected, in control samples RefO and rTBHQ, it was at a very low level and amounted to 0.002 and 0.006, respectively. For all samples a similar tendency in the change in the color index under the influence of heating was observed. At 170 °C the color index increased in all

blends, except for RO25%, which exhibited a decrease of over one-third of the initial value. The greatest change in the color index was observed in RefO samples, where this value increased by almost 20 times. The smallest increase in the color index was observed in RO5% and CO25% samples. The rise in the color index at 170 °C may be elucidated by the accumulation of colored TAG degradation products and indicates a progressive deterioration of the sample quality during heating. However, at 200 °C the color index was lower than at 170 °C and comparable to (CO5%, AO5%, and AO25%) or even lower (RO5%, RO25%, and CO25%) than for unheated blends. This decline likely resulted from chlorophyll decomposition. It is especially visible in the RO25% sample, in which the chlorophyll decomposition effect at 170 °C outweighed the colored TAG degradation product effect due to its high initial chlorophyll content in RO25%. Detailed data on the color index are presented in Table S3 (Supplementary Materials). The reduction in chlorophyll pigments after hot plate heating and microwave heating in mustard and olive oil was confirmed by visible spectra analysis performed by Khan et al. [70].

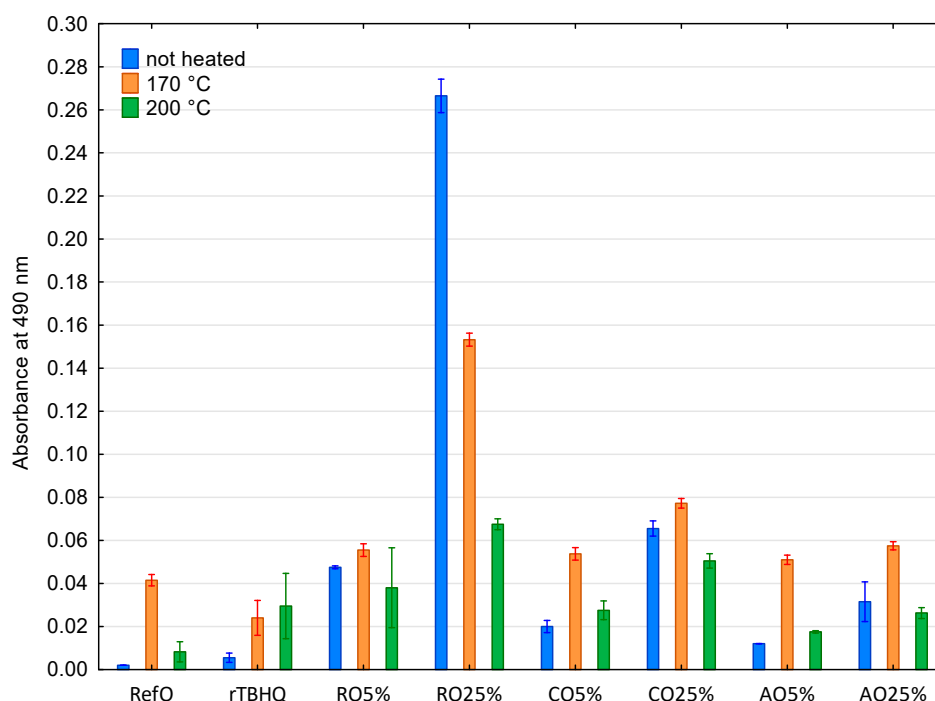


Figure 3. The color index in blends unheated and heated at 170 and 200 °C. RefO—refined rapeseed oil; rTBHQ—refined rapeseed oil with the addition of tert-butylhydroquinone; RO5%—a blend of refined rapeseed oil and 5% cold-pressed rapeseed oil; RO25%—a blend of refined rapeseed oil and 25% cold-pressed rapeseed oil; CO5%—a blend of refined rapeseed oil and 5% cold-pressed coriander seed oil; CO25%—a blend of refined rapeseed oil and 25% cold-pressed coriander seed oil; AO5%—a blend of refined rapeseed oil and 5% cold-pressed apricot kernel oil; AO25%—a blend of refined rapeseed oil and 25% cold-pressed apricot kernel oil.

Other authors [71] examined color index changes during frying of distilled olive pomace oil with or without additives. They observed that the color index increase was higher in the sample without additives than in the sample with squalene but lower compared to the sample with mono- and diglyceride addition. Aladedunye and Przybylski [72] concluded that the darkening of oils during frying may be attributed to the formation of nonenzymatic browning compounds. However, the formation of some carotenoid oxidation products, polymerized tocotrienols, and polymerized acylglycerols may contribute to the higher UV absorbance. Also, nonvolatile decomposition products [NVDPs] and α -

β -unsaturated carbonyl compounds formed during oxidation and thermal decomposition of unsaturated fatty acids are considered as pigments responsible for the oil darkening [73]. Lazarick [74] stated that the oil darkening may result from the production of the polypyrrolic polymers and the short-chain aldehydes.

3.5. Total Polar Compounds (TPCs) and Oxidized TAG Monomer (oxTAG) Content

Total polar compounds (TPCs) represent non-volatile degradation products formed through oxidation and hydrolysis of TAG, which exhibit greater polarity than the unmodified TAG. They are among the most reliable and widely recognized indicators of frying fat quality worldwide. Many countries have established TPC content limits in frying oils, ranging from 24% to 30% [75,76].

The level of TPC did not exceed the recommended value in any samples. The refined rapeseed oil without additives (RefO) had the highest TPC content, both heated at 170 °C and 200 °C (7.78 and 12.34%, respectively) (Table 2). At 170 °C, the RefO sample differed significantly from all the others except the AO25% sample. However, at 200 °C only the RO5%, CO5%, and CO25% samples had significantly lower TPC content than the RefO sample. This indicates that heating at higher temperatures and the resulting more advanced degradation of oils made the samples more similar to each other. This is probably due to the progressive loss of bioactive compounds and is consistent with the correlation analysis and principal component analysis (PCA).

Table 2. The total polar compound content [%] in unheated and heated blends and its increase after heating.

	Unheated	170 °C	Increase in TPC Content After Heating at 170 °C	200 °C	Increase in TPC Content After Heating at 200 °C
RefO	2.31 ± 0.11 aA	7.78 ± 1.00 cB	5.47	12.34 ± 1.19 cC	10.03
rTBHQ	2.04 ± 0.57 aA	5.02 ± 1.24 abB	2.98	11.24 ± 0.35 bcC	9.20
RO5%	2.71 ± 0.21 aA	3.61 ± 0.57 aA	0.90	8.45 ± 0.83 aB	5.74
RO25%	2.19 ± 0.67 aA	4.17 ± 0.51 aA	1.98	10.60 ± 1.57 abcB	8.41
CO5%	3.54 ± 1.21 aA	4.96 ± 0.86 abA	1.42	9.79 ± 1.25 abB	6.25
CO25%	3.03 ± 1.71 aA	4.77 ± 0.47 abA	1.74	9.37 ± 0.99 abB	6.34
AO5%	2.94 ± 0.45 aA	3.11 ± 0.47 aA	0.17	11.07 ± 1.27 bcB	8.13
AO25%	4.65 ± 0.04 aA	6.54 ± 0.66 bcB	1.89	10.36 ± 0.73 abcC	5.71

RefO—refined rapeseed oil; rTBHQ—refined rapeseed oil with the addition of tert-butylhydroquinone; RO5%—a blend of refined rapeseed oil and 5% cold-pressed rapeseed oil; RO25%—a blend of refined rapeseed oil and 25% cold-pressed rapeseed oil; CO5%—a blend of refined rapeseed oil and 5% cold-pressed coriander seed oil; CO25%—a blend of refined rapeseed oil and 25% cold-pressed coriander seed oil; AO5%—a blend of refined rapeseed oil and 5% cold-pressed apricot kernel oil; AO25%—a blend of refined rapeseed oil and 25% cold-pressed apricot kernel oil. TPCs—total polar compounds. The values for samples of unheated blends are the means of two determinations ± SDs. Values for heated samples are the means of four determinations ± SDs. Means in the same column followed by different lowercase letters indicate significant differences ($p < 0.05$) between samples treated in the same conditions. Means in the same row followed by different capital letters indicate significant differences ($p < 0.05$) between samples at different treatment temperatures.

RefO sample also exhibited the highest increase in TPC content under heating conditions at both temperatures (5.47% at 170 °C and 10.03% at 200 °C). It indicates that the addition of cold-pressed oils significantly reduced oxidation during thermal treatment, although their protective effects varied. The AO5% sample exhibited the lowest TPC content (3.11%) and the smallest increase in this parameter (0.17%) at a temperature of 170 °C.

Among samples heated at 200 °C, the lowest TPC level was found in the RO5% sample (8.45%), while its lowest increase was in the AO25% sample (by 5.71%).

Notably, rTBHQ samples were characterized by the second-highest increase in TPC, at both 170 °C and 200 °C (by 2.98 and 9.20%, respectively). This means that the additions of cold-pressed oils were more effective in reducing the TPC increase than the addition of the synthetic antioxidant TBHQ.

Oxidized TAG monomers (oxTAGs) are one of TPC fractions, generated by the addition of an extra oxygen atom to at least one unsaturated bond in one or more of the fatty acids chains, which results in the formation of oxygenated functional groups. Their molecular weight is close to the original, unmodified TAG [77]. The results of the analysis of oxTAG content in blends are presented in Table 3. The oxTAG content in unheated samples ranged from 18.20 to 43.28 mg/g of oil. Among the samples heated at 170 °C, the highest oxTAG content was noted in the RefO (75.84 mg/g of oil) and AO25% (61.84 mg/g of oil) samples. The RefO sample differed significantly from the others, except for the AO25% sample. The lowest oxTAG content was noted in the AO5% (29.04 mg/g of oil) and RO5% (34.80 mg/g of oil) samples. The remaining samples were characterized by a similar oxTAG in the range from 41.14 to 49.06 mg/g of oil. In the samples heated at 200 °C, the highest content of oxTAG was characteristic of the RefO sample (113.77 mg/g of oil), and it differed significantly from the RO5% sample with the lowest content of oxTAG (73.20 mg/g of oil) and two other samples CO5% and CO25%.

Table 3. The content of oxidized TAG monomers [mg/g oil] in unheated and heated blends and its increase after heating.

	Unheated	170 °C	Increase in oxTAG Content After Heating at 170 °C	200 °C	Increase in oxTAG Content After Heating at 200 °C
RefO	20.87 ± 2.14 aA	75.84 ± 10.31 cB	54.97	113.77 ± 9.53 cC	92.90
rTBHQ	18.20 ± 5.65 aA	49.06 ± 12.29 abB	30.86	98.76 ± 4.06 bcC	80.56
RO5%	24.94 ± 1.51 aA	34.80 ± 6.11 aA	9.86	73.20 ± 10.35 aB	48.26
RO25%	20.17 ± 6.38 aA	41.14 ± 4.89 aA	20.97	91.92 ± 12.20 abcB	71.75
CO5%	31.66 ± 12.01 aA	45.99 ± 10.02 abA	14.33	87.85 ± 11.49 abB	56.19
CO25%	28.61 ± 16.04 aA	46.19 ± 4.99 abA	17.58	84.99 ± 9.80 abB	56.38
AO5%	27.64 ± 4.21 aA	29.04 ± 4.61 aA	1.40	101.09 ± 14.49 bcB	73.45
AO25%	43.28 ± 0.27 aA	61.84 ± 6.09 bcA	18.56	90.81 ± 9.42 abcB	47.53

RefO—refined rapeseed oil; rTBHQ—refined rapeseed oil with the addition of tert-butylhydroquinone; RO5%—a blend of refined rapeseed oil and 5% cold-pressed rapeseed oil; RO25%—a blend of refined rapeseed oil and 25% cold-pressed rapeseed oil; CO5%—a blend of refined rapeseed oil and 5% cold-pressed coriander seed oil; CO25%—a blend of refined rapeseed oil and 25% cold-pressed coriander seed oil; AO5%—a blend of refined rape-seed oil and 5% cold-pressed apricot kernel oil; AO25%—a blend of refined rapeseed oil and 25% cold-pressed apricot kernel oil. oxTAG—oxidized TAG monomers. The values for samples of unheated blends are the means of two determinations ± SDs. Values for heated samples are the means of four determinations ± SDs. Means in the same column followed by different lowercase letters indicate significant differences ($p < 0.05$) between samples in the same conditions. Means in the same row followed by different capital letters indicate significant differences ($p < 0.05$) between samples at different treatment temperatures.

The results from this study indicate oil degradation during heating at frying temperature, which is significantly more advanced at 200 °C than at 170 °C. In the initial stages of lipid oxidation, primary oxidation products, which are lipid hydroperoxides, are formed. At high temperature they decompose to secondary oxidation products like aldehydes, ketones, and alcohols, which leads to the formation of TPC and oxTAG [78]. However, a smaller increase in TPC and oxTAG content in blends compared with control samples indicates that the addition of cold-pressed oils could be effective in limiting TAG

oxidation. This may be attributed to the influence of the fatty acid profile because blends with coriander seed oil and apricot kernel oil showed a lower degree of unsaturation determined by the CIV compared to the other samples. These results are consistent with the data presented in previous studies [79–81]. It may be a result of the greater susceptibility of PUFAs to degradation under conditions of high temperature and contact with oxygen. However, this is only a partial explanation since the blends with cold-pressed rapeseed oil had a similar degree of unsaturation to refined rapeseed oil but also lower contents of TPC and oxTAG. Furthermore, the fatty acid profile does not explain the variability in the level of TPC and oxTAG between the individual blends with highly monounsaturated cold-pressed oils.

The observed variability may result from the action of bioactive compounds present in cold-pressed oils, such as tocopherols, which act as chain-breaking antioxidants, mainly by the hydrogen atom transfer (HAT) mechanism. It caused the first steps of TAG oxidation processes to be interrupted and radicals to be neutralized. Consequently, the formation of primary oxidation products as well as secondary oxidation products was slowed, which led to a lower level of TPC [82,83]. Moreover, the ratio of tocopherol homologs may be crucial for the thermal and oxidative stability of oil [84,85]. Our previous study [61] showed a significant tocopherol reduction after heating. It may be a result both of thermal degradation of tocopherols and their active consumption as antioxidants during oxidation. However, the results of correlation analysis and PCA indicate that the second mechanism is particularly important. Tocopherol degradation is strongly dependent on temperature. At lower temperature, in the range between 30 and 100 °C, this process occurs slowly, and several weeks or months are required to observe substantial depletion [86]. At medium temperature, in the range between 140 and 170 °C, degradation of tocopherols is markedly accelerated and occurs within hours [87]. At high temperatures, around 200 °C, which is typical for frying, almost total degradation of tocopherols may be observed after several minutes [61].

The inhibitory effect on lipid oxidation may also result from the influence of phenolic compounds, which occur in abundance in cold-pressed oils, according to many publications [88–90]. Numerous studies have shown that oils with a higher content of native or added phenolic compounds exhibited higher stability in accelerated aging tests [91,92] and during frying [32,66,93]. This is mainly related to the ability of phenolic compounds to quench free radicals by donating a hydrogen atom or an electron. It should be noted that the structure of phenolic compounds is of great importance, including the number and position of hydroxyl groups, the degree of methylation, the presence of other substituents, glycosylation, and the presence of a double bond between C2 and C3 (in the C ring of flavonoids) [94,95]. There is no data in the literature on the composition of phenolic compounds in coriander seed oil. However, their composition was examined in coriander seed extract [96]. Ten phenolic compounds were identified, and chlorogenic acid had the dominant share (490.56 µg/g of extract), followed by vanillic acid (273.23 µg/g of extract) and ferulic acid (239.21 µg/g of extract). The strong antioxidant properties [97] of ferulic and vanillic acids result from the presence of a hydroxyl group substituted in the para-position to the side chain with a conjugated double bond. This arrangement enables electron delocalization in the entire phenoxyl radical molecule, which has a beneficial effect on its stability and thus improves the antioxidant properties of the phenolic compound.

The antioxidant activity of our blends was described in our previous study [61]. The highest antioxidant activity measured by DPPH and ABTS was found in the rTBHQ sample. It was followed by blends with cold-pressed rapeseed oil, considering DPPH, and by blends with coriander and apricot oils regarding ABTS. The DPPH assay applies a radical dissolved only in organic media and therefore suits lipophilic systems, whereas the ABTS assay is used to determine scavenging ability in both hydrophilic and lipophilic

antioxidant systems. Therefore, it may be assumed the protective effect of cold-pressed rapeseed oil results mainly from the activity of lipophilic antioxidants. In the case of coriander and apricot oils, it could be the effect of both hydrophilic and lipophilic antioxidant activity. In the publication by Ramadan et al. [98], 10 oils were examined regarding the antioxidant activity measured by the DPPH test. It was found that coriander oil was the most effective in quenching free radicals. According to the authors, the differences in the antioxidant properties of the oils may result from differences in the content and composition of polar bioactive components of the unsaponifiable fraction, differences in the structure of potential phenolic antioxidants in the oils, synergistic interactions between polar bioactive substances and other components of the oils, or differences in the kinetics of the antioxidant reactions occurring in the oils. All these factors may contribute to the radical quenching efficiency of the oils.

Another factor that may affect the inhibition of TAG oxidation in blends with coriander seed oil is the presence of essential oil in these samples. It has been proven [99] that the addition of coriander essential oil to sunflower oil reduces the formation of TPC and TAG polymers during deep frying. It was shown that coriander essential oil can be a rich source of phenolic antioxidants like eugenol and non-phenolic substances such as linalool, limonene, and γ -terpinene, which may also exhibit antioxidant properties [100].

3.6. Triacylglycerol (TAG) Polymer Content

Triacylglycerol (TAG) polymers are formed via a polymerization reaction by connecting two, three, or more TAG molecules, which are named dimers, trimers, and oligomers, respectively. They may be polar or non-polar, depending on the presence or absence of oxidized functional groups. They have complex structures and are formed in more advanced stages of oil degradation. Their molecular weight is higher than the original, unmodified TAG. They are considered a good indicator of frying oil quality [77,101]. Some countries have established limits of TAG polymers, ranging between 10 and 16 g/100 g oil [75]. TAG polymers disturb technological processes by prolonging the frying process and increasing viscosity. They increase the fat content of the dish, which is adverse from a nutritional perspective. Moreover, consuming TAG polymers may have harmful effects on health due to damage to the intestinal mucosa and may contribute to cancer [102]. TAG dimers were the only polymer fraction detected in this study and only in the samples heated at 200 °C. The results of the analysis of TAG dimers in blends are presented in Table 4. The content of TAG dimers did not exceed the upper permissible limit, 16 g/100 g of oil in any sample, but was above the recommended lower permissible limit, 10 g/100 g of oil in three samples, namely, RefO, rTBHQ, and RO25%. However, there were no statistically significant differences between these three samples and the others, except for the CO25% sample with the lowest dimer content (6.11 mg/g oil). This was less than 59% of TAG dimer content in the RefO sample. It may be concluded that 25% coriander oil addition delayed TAG polymerization. Previous studies revealed that the use of antioxidants in frying oil may play an important role in mitigating the degradation of polymers and other degradation products during the frying process [13,103,104]. However, the effectiveness of antioxidants in preventing polymer formation may be influenced by factors such as the type of antioxidant, the frying temperature, and the duration of the frying process [13,103,104].

Table 4. The content of TAG dimers [mg/g oil] in unheated and heated blends.

	Unheated	170 °C	200 °C
RefO	n/d	n/d	10.51 ± 1.99 a
rTBHQ	n/d	n/d	10.44 ± 0.65 a
RO5%	n/d	n/d	7.98 ± 0.37 ab

RO25%	n/d	n/d	10.55 ± 2.91 a
CO5%	n/d	n/d	7.24 ± 1.37 ab
CO25%	n/d	n/d	6.11 ± 2.12 b
AO5%	n/d	n/d	7.20 ± 0.83 ab
AO25%	n/d	n/d	8.91 ± 2.43 ab

n/d—not detected; RefO—refined rapeseed oil; rTBHQ—refined rapeseed oil with the addition of tert-butylhydroquinone; RO5%—a blend of refined rapeseed oil and 5% cold-pressed rapeseed oil; RO25%—a blend of refined rapeseed oil and 25% cold-pressed rapeseed oil; CO5%—a blend of refined rapeseed oil and 5% cold-pressed coriander seed oil; CO25%—a blend of refined rapeseed oil and 25% cold-pressed coriander seed oil; AO5%—a blend of refined rapeseed oil and 5% cold-pressed apricot kernel oil; AO25%—a blend of refined rapeseed oil and 25% cold-pressed apricot kernel oil. The values for samples of unheated blends are the means of two determinations ± SDs. Values for heated samples are the means of four determinations ± SDs. Means in the same column followed by different letters indicate significant differences ($p < 0.05$) between samples.

Harzalli et al. [105] observed that the addition of olive mill wastewater extract to refined sunflower oil reduces the formation of TAG polymers and aldehydes. Similarly, olive oil with the extract had lower levels of TAG polymers compared to refined sunflower oil. Surprisingly, olive oil without the extract showed lower content of TAG polymers and aldehydes than olive oil enriched by the extract. This indicates that substances naturally occurring in oils may be more effective in limiting thermal TAG degradation than exogenous additives. Additionally, they showed that the highest percentage of polyunsaturated fatty acids in refined oil was associated with a greater tendency to form polymeric compounds.

Other authors reported interesting results using ^1H NMR and electron spin resonance techniques [106]. It was shown through ^1H NMR spectra that heated palm oil had a higher percentage of the allyl acyl group and was more prone to the formation of non-polar dimeric TAG compared to refined palm kernel oil and refined coconut oil. In addition, electron spin resonance spectra indicated that alkyl radicals were more predominant than alkoxy radicals in heated palm oil. In contrast, refined palm kernel oil and refined coconut oil were predisposed to the generation of alkoxy radicals during thermal treatment. The authors explained that this discrepancy may be a result of differences in fatty acid composition.

Based on a study [107] of TAG polymer content in oxidized soybean oil at frying temperatures, it was suggested that ester bonds are primarily responsible for the polymerization of oils during frying. This polymerization process is evidenced by increased ester values and specific NMR signals.

3.7. Correlation Analysis

A significant, strong, negative correlation between total tocopherols and TPC, as well as between total tocopherols and oxTAG content ($r = -0.7890$ and -0.7915 , respectively, $p < 0.05$), was found (Table 5). Interestingly, we found that plastochroman-8 (PC-8) content showed the strongest significant negative correlation among tocopherols with TPC and oxTAG content ($r = -0.8173$ and -0.8155 , respectively, $p < 0.05$), despite the relatively low initial concentration. PC-8 has been proven to be an effective singlet oxygen scavenger both in vitro and in vivo, and it was more active than tocopherols in the inhibition of the peroxidation reaction [108]. γ -tocopherol also exhibited a very strong negative correlation with TPC and oxTAG (-0.8094 and -0.8058 , respectively), which was stronger than that observed for α -tocopherol (-0.7237 and -0.7324 , respectively) and the remaining tocopherol homologs. This finding indicates a significant role of γ -tocopherol in limiting oxidative processes occurring in the studied oils and suggests that its effect was more pronounced than that of α -tocopherol. It should be noted that both α -tocopherol and γ -

tocopherol were the most abundant tocopherols present in the oils. The ABTS analysis results had a significant, negative correlation with TPC and oxTAG content ($r = -0.7514$ and -0.7552 , respectively, $p < 0.05$), which was higher than the correlation of DPPH with TPC and with oxTAG content. The DPPH assay typically uses an organic solvent and therefore is appropriate for lipophilic systems, whereas the ABTS assay may be carried out both in hydrophilic and lipophilic systems [109]. The results may indicate a synergistic interaction between hydrophilic and hydrophobic antioxidants, which is in agreement with our previous study [61].

Table 5. Pearson correlation coefficients (r) between minor compound content and antioxidant activity relative to the content of oil thermal degradation products.

	TPC	oxTAG	Dimers TAG
α -tocopherol	−0.7237	−0.7324	−0.5748
β -tocopherol	−0.5247	−0.5191	−0.4814
γ -tocopherol	−0.8094	−0.8058	−0.7367
δ -tocopherol	−0.6578	−0.6416	−0.7071
PC-8	−0.8173	−0.8155	−0.7131
total tocopherols	−0.7890	−0.7915	−0.6744
total phytosterols	−0.4557	−0.4571	−0.3046
DPPH	−0.5893	−0.5920	−0.4809
ABTS	−0.7514	−0.7552	−0.6503

Significance at $p < 0.05$.

3.8. Principal Component Analysis (PCA)

PCA calculation was performed based on 21 variables, which are presented in the present and previous study [61]. The first four PCs were extracted with eigenvalues higher than 1 (Kaiser's rule). Together, they explained over 90% of the total variance, and it was 48.84, 25.45, 9.94, and 6.34.

In Figure 4A, PC1 was positively correlated with polar compound content (0.8523), oxidized TAG monomer content (0.8495), and TAG dimer content (0.7578) and negatively correlated with PC-8 (−0.9364), γ -tocopherol (−0.9306), tocopherols (−0.8932), ABTS (−0.8727), α -tocopherol (−0.8173), and DPPH (−0.7442). PC1 was ascribed to the x-axis, along which the samples (Figure 4B) were distributed from unheated (left side of the axis) through heated at 170 °C (mainly in the center), to heated at 200 °C (right side of the axis). It may be assumed that PC1 was related to the gradual oil deterioration during heating. PC2 was mainly characterized by the PUFA/SFA ratio (0.7500), PUFAs (0.7208), as well as β -tocopherol (−0.8475), δ -tocopherol (−0.7957), and TI (−0.7360). Figure 4B shows that the samples were distributed into three major clusters, which reflected differences in heat treatment. Cluster I (green color) contained unheated samples with the highest content of total tocopherols but the lowest of TPC, oxTAG, and TAG dimers. Cluster II (blue color) grouped samples heated at 170 °C. Cluster III (red color) comprised samples heated at 200 °C, with the most advanced deterioration, including lower content of minor compounds but higher content of degradation products. All clusters were located far from each other, which indicates that heating caused significant changes at both temperatures. CO25% blends unheated and heated at 170 and 200 °C were outliers, mainly due to differences in fatty acid composition. Surprisingly, rTBHQ heated at 170 °C was located among unheated samples, which indicates that the synthetic antioxidant was highly effective in reducing the degradation process. However, rTBHQ heated at 200 °C was placed together with other samples heated at 200 °C. This means that at higher temperature, the synthetic antioxidant lost its protective properties and was less effective than, for example, the additive CO25%.

PC3 and PC4, presented in Figure 4C,D, together explained 16.28% of the total variability of the results. In Figure 4C, most variables were clustered near the center of the plot. PC3 was mainly positively correlated with the phytosterol content (0.7020), whereas PC4 was mainly positively correlated with the color index (0.6970). Figure 4D shows that the samples located on the left side of the x-axis (PC3) were characterized by lower phytosterol content, and samples located on the top of the y-axis (PC4) were characterized by a higher color index.

The grouping of blends in the study was determined mainly by the level of degradation products and the content of tocochromanols, particularly γ -tocopherols and PC-8. The fatty acid profile and CIV were also important; however, in this study their impact was less pronounced, probably due to the similar proportions of MUFAs, PUFAs, and SFAs among the blends. The findings indicate that the blend formulation should account for not only the composition of fatty acids but also the content and selection of antioxidants like tocochromanols.

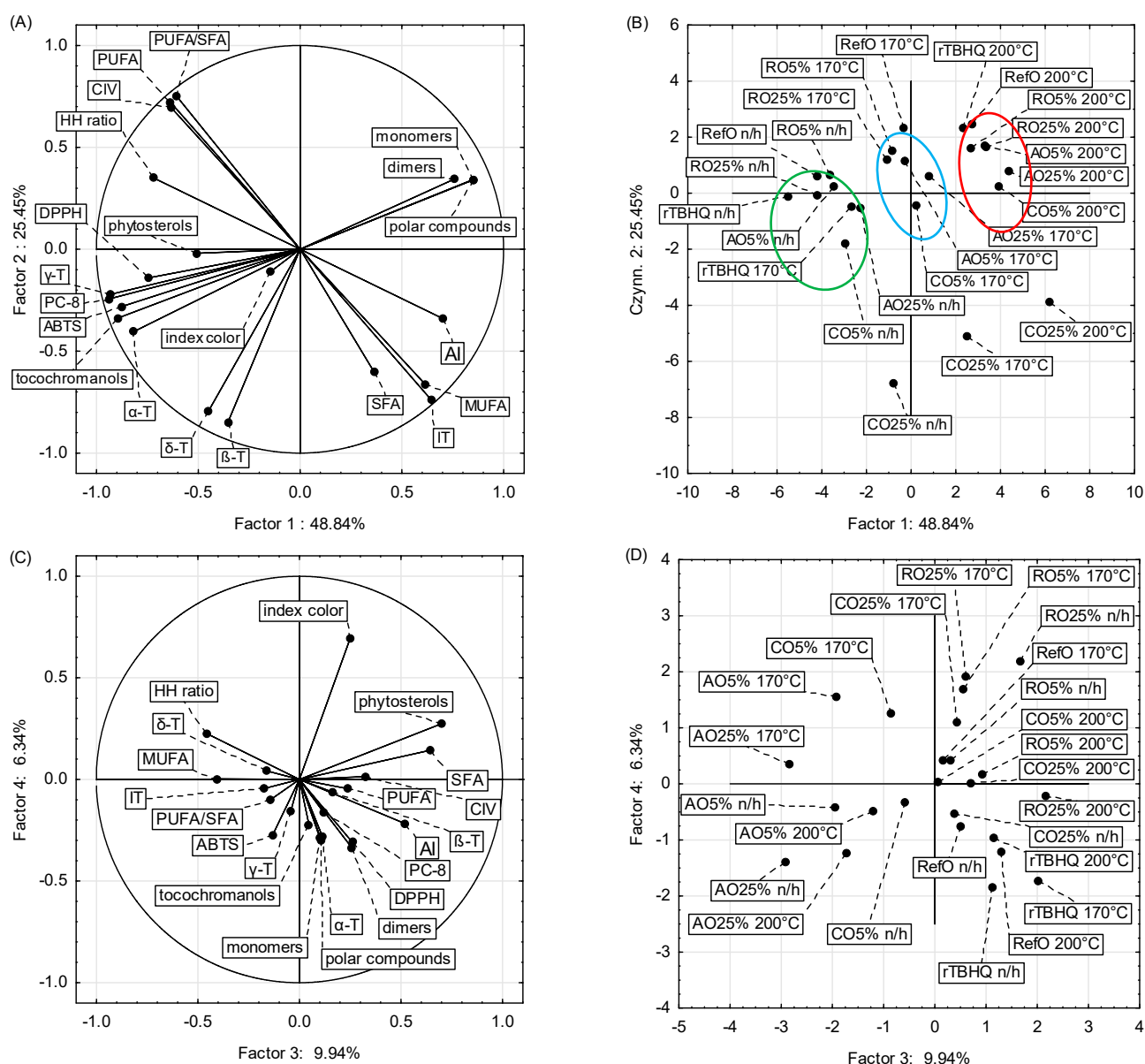


Figure 4. Score plots and loading plots for PC1 and PC2 (A,B) and PC3 and PC4 (C,D) from principal component analysis (PCA), illustrating the relationship between unheated (n/h) and heated at 170 and 200 °C samples. Green circles—Cluster I, blue circles—Cluster II, red circles—Cluster III.

4. Conclusions

The effect of refined rapeseed oil and cold-pressed oil blending on stability of oil at temperatures typical for frying was investigated (at 170 and 200 °C). High temperature was shown to promote oil degradation via oxidation and TAG polymerization, and it was more intense at 200 °C. The addition of cold-pressed oils limited the increase in the contents of TPC and oxTAG during heating at both temperatures and was more effective than TBHQ. This was particularly visible at 200 °C, where TBHQ lost much of its protective properties, while blends with cold-pressed oils still had much lower contents of TPC and oxTAG than refined rapeseed oil. Only the CO25% sample had a statistically significantly lower TAG dimer content than refined rapeseed oil and the control sample with TBHQ. These results showed that 25% coriander oil addition slowed the TAG polymerization process. It can be concluded that cold-pressed oils have great potential to replace synthetic antioxidants and to increase the thermal stability of frying oils. However, individual types of cold-pressed oils differ in their protective properties. Statistical analysis indicates that tocopherols, especially PC-8 and γ -tocopherol, may effectively limit the thermal degradation of oils. An increase in the color index at 170 °C indicated accumulation of colored TAG degradation products and a deterioration of sample quality. Heating at 200 °C led to a decrease in the color index and was probably caused by chlorophyll degradation. Under the conditions of our study, parameters such as TPC and the content of tocopherols appear to be useful indicators for evaluating of mixtures dedicated to high-temperature applications.

Blends of cold-pressed rapeseed and coriander oils can be used in home and catering settings to produce fried products with improved nutritional quality. The tested blends may be used in the fried snack industry, such as in chips, French fries, nuggets, or breaded products.

Study limitations include the single heating cycle and lack of sensory analysis. Future studies could focus on quantifying volatile off-flavors via GC-MS and sensory analysis of blends before and after heating. Future work could also evaluate blends during repeated and continuous frying, deep frying, and storage at room and refrigerator temperatures. Moreover, further research is required to understand the complex process of degradation of triacylglycerols and other oil components and the role of bioactive substances.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/app16031589/s1>, Table S1. Shares of saturated, monounsaturated, and polyunsaturated fatty acids and calculated iodine value in unheated and heated blends. Table S2. Indices of lipid nutritional quality in unheated and heated blends. Table S3. The color index in unheated and heated blends.

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