Effect of Industrial Refining Process on Fatty Acid, Sterol, Volatile Compound Profile and 3-MCPD Ester Content of Canola and Corn Oils

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Abstract: The study reports the changes in fatty acid and sterol composition; as well as volatile and 3-monochloropropane-1,2-diol (3-MCPD) ester content of two commercial vegetable oils at different steps of refining process. Canola and corn oils were collected from neutralization, bleaching, winterization and deodorization stages of a chemical refining plant and oil samples were evaluated for fatty acid, sterol, volatile compounds and 3-MCPD ester contents. Fatty acid and sterol profiles were determined using IUPAC and AOCS Official Methods respectively and 3-MCPD ester content was determined using DGF C VI 18 (10) Official Method. Results have shown that total sterol contents decreased throughout the process by 15.22% and 42.57% for canola and corn oils, respectively. Total volatiles of canola oil decreased gradually during refining, however corn oil had significant increases at bleaching step. 3-MCPD ester contents were between 0.19-0.26 mg kg^{-1} for corn and 0.20-0.48 mg kg^{-1} for canola oils. Deodorization was found to be the most influential refining stage for formation of 3-MCPD esters.

Keywords: 3-MCPD ester, fatty acid, refining, sterol, volatile compounds

Endüstriyel Rafinasyon İşleminin Kanola ve Mısır Yağlarının Yağ Asidi, Sterol, Uçucu Bileşen Profili ve 3-MCPD Ester İçeriğine Etkisi

Öz: *Çalışma, farklı rafinasyon aşamalarındaki ticari bitkisel yağların 3-monokloropropan-1,2-diol (3-MCPD) ester miktarı ve uçucu bileşen miktarının yanısıra yağ asidi ve sterol bileşimlerinde meydana gelen değişiklikleri rapor etmektedir. Kanola ve mısır yağları, kimyasal rafinasyon gerçekleştiren bir işletmenin nötralizasyon, ağartma, vinterizasyon ve deodorizasyon aşamalarından temin edilmiş ve yağ asidi, sterol, uçucu bileşenler ve 3-MCPD ester içerikleri yönünden değerlendirilmiştir. Yağ asidi ve sterol profilleri sırasıyla IUPAC ve AOCS Resmi Metotları kullanılarak, 3-MCPD ester miktarı ise DGF C VI 18 (10) Resmi Metodu kullanılarak belirlenmiştir. Çalışma sonuçları sterollerin toplam miktarlarının işlem boyunca kanola ve mısır yağları için sırasıyla %15.22 ve %42.57 düzeylerinde azaldığını göstermiştir. Kanola yağının toplam uçucu madde miktarı rafinasyon sırasında kademeli olarak azalmıştır, ancak mısır yağında ağartma aşamasında önemli derecede artış olmuştur. 3-MCPD ester miktarı mısır yağı için 0.19-0.26 mg kg^{-1}, kanola yağı için ise 0.20-0.48 mg kg^{-1} olarak belirlenmiştir. Deodorizasyonun 3-MCPD ester oluşumu için en önemli basamak olduğu tespit edilmiştir.*

Anahtar kelimeler: *3-MCPD ester, rafinasyon, sterol, uçucu bileşenler, yağ asidi*

INTRODUCTION

Crude vegetable oils contain some impurities such as free fatty acids, phosphatides, waxes, oxidation products, color pigments and odorants which impair organoleptic properties and stability. Therefore most edible oils are refined before consumption. There are several stages in refining process, namely, degumming, neutralization, bleaching and deodorization and each step affects the composition of the oil. There are a number of reports evaluating the effect of refining process on various constituents of different types of oils. Cottonseed oil has been evaluated for the change in tocopherol, sterol content and fatty acid composition (El-Mallah et al., 2011); sunflower oil for tocopherol content (Naz et al., 2011; Tasan and Demirci, 2005; Alpaslan et al., 2001), *trans* fatty acids (Tasan and Demirci, 2003), polycyclic aromatic hydrocarbons (Teixeira et al., 2007); soybean oil for phospholipid, chlorophyll and tocopherol content (Jung et al., 1989), sterol (Johansson and Hoffmann, 1979), steradien, steryl ester, polymeric glycerides (Ferrari et al., 1996), conjugated dien content (Bachari-Saleh et al., 2013); coconut oil for fatty acid composition (Petrauskaitè et al., 2000); tea seed oil for fatty acid composition, sterol, α-tocopherol, vitamin D_3 and squalene content (Wei et al., 2015); safflower oil for sterol and tocopherol content (Ortega-García et al., 2006); rice bran oil for oryzanol content (Krishna et al., 2001) fatty acid, diglyceride, tocopherol and tocotrienol content (Hoed et al., 2006); wheat germ oil for tocopherol and fatty acids (Wang and Johnson, 2001); olive oil for wax, fatty alcohol (Tubaileh et al., 2002), phenolic compound distribution (Garcia et al., 2006); hazelnut oil for fatty acids, tocopherol and sterols (Karabulut et al., 2005); canola oil for fatty acids, polar compounds (Farhoosh et al., 2009); rapeseed oil for 4-vinylsyringol and phenolics (Kraljić et al., 2015); Moringa oleifera seed oil for density, viscosity, saponification value, fatty acids and oxidation indices (Sánchez-Machado et al., 2015); peanut, sunflower, maize, palm nut and lampante olive oils for phytosterol oxidation products (Bortolomeazzi et al., 2003). Although substantial effort has been paid to

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determine the effect of refining on some minor compounds of various vegetable oils, there is no information on the influence of refining steps on volatile components of vegetable oils. Hence, the first aim of the work was to investigate the change in volatile components together with fatty acids and individual sterols.

3-Monochloropropane-1,2-diol (3-MCPD) is a process contaminant which may be formed at excessive temperatures in the presence of chloride. It can be found either in free or ester forms in different foods. There are various factors promoting the formation of 3-MCPD esters during oil refining (Matthäus et al., 2011; Pudel et al., 2011) and therefore each one of the refining stage may have incompatible effect on the formation of ester-linked 3-MCPD. Hence the refining process was attributed as target operation for mitigation strategies (Craft et al., 2012). Different vegetable oils have different capabilities to form 3-MCPD esters (Pudel et al., 2011). Additionally there's scarce information in literature about the impact of different processing conditions on the formation of 3-MCPD esters. Because the first step of characterization and reduction of 3-MCPD esters lies in the knowledge of their detection during different processes, in the current study, individual steps of oil refining are evaluated for their potency to form ester bound 3-MCPD in order to bring more clearance into the further characterization and mitigation studies.

MATERIAL AND METHODS

Oil Samples

Canola and corn oil samples were kindly supplied from an industrial refining plant.

Refining Procedures

Canola and corn oils were obtained from processing lines of refineries. Both types of oils were processed in the same way, in four different steps: degummimg-neutralizing, bleaching, winterization and deodorization. Chemical refining was performed as follows: In the first step, the crude oil was heated up to 80°C. Phosphoric acid (85%) was added at 0.05% level as degumming agent and the mixture was stirred for 5-10 minutes. Afterwards, oil was mixed with 15-16°Be' NaOH for 15-20 minutes. The soapstock was separated from the oil by centrifuging and the oil was washed with 2% water and centrifuged again. The neutralized oil was then dried with vacuum driers to remove the remaining water present in the oil. In bleaching step, neutralized oil was heated to 100-110°C and 0.4-0.8% of bleaching earth was added. The mixture was heated for 30-45 min and filtered. The filtration was accomplished at 100-120°C under 70 mbar vacuum to remove bleaching earth and adsorbed constituents from the oil. In the next step, winterization was achieved by cooling the oil to 7-10°C and then filtering to discard the waxes and saturated fraction. Finally, the oil was deodorized at 155-245°C under 2.5-4 mbar vacuum to eliminate the volatile compounds. The representative samples of 250 mL were stored at -18°C in nitrogen atmosphere until analysis.

Analyses

Fatty acid composition

The fatty acid methyl esters were prepared according to International Union of Pure and Applied Chemistry (1987). A gas chromatograph GC 2010 (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector (T = 240°C), split/splitless injector (T = 290°C) and DB-23 fused silica capillary column (60 m x 0.25mm i.d. and 0.25 µm film thickness) (J&W Scientific) was employed to analyze individual fatty acids. Oven temperature was 195°C. Nitrogen was used as carrier gas with a flow rate of 1 mL/min and the split ratio was 80:1.

Sterol composition

Sterol contents of oil samples were determined according to AOCS Official Method Ch 6-91 (2003). Sterol derivatives were analyzed using a gas chromatography instrument (Shimadzu, Kyoto, Japan) equipped with a split/splitless injector (T = 280°C), flame ionization detector (T = 290°C) and HP-5 fused silica capillary column (30 m, 0.25 mm i.d. and 0.25 mm film thickness) (Chrom Tech., Apple Walley, MN, USA) was employed for chromatographic elution. 5α-cholestan-3β-ol was used as internal standard. Nitrogen was the carrier gas with a flow rate of 0.8 mL/min and the split ratio was 50:1.

Volatile compound analysis

Static headspace gas chromatography-mass spectrometry (SHSGC-MS) was employed to determine the volatile profile of oils. The headspace of oils were analyzed by Agilent 7697A model (Agilent Technologies, Santa Clara, CA, USA) headspace sampler. The headspace was connected to a 7820A model (Agilent Technologies, Santa Clara, CA, USA) gas chromatograph and associated with a mass selective detector of Agilent 5975 model (Agilent Technologies, Santa Clara, CA, USA). A 10 mL of sample was placed in a 20 mL vial which is sealed with poly(tetrafluoroethylene) (PTFE)/silicone septum. The extraction conditions were as follows: Oven temperature, 120°C; loop temperature, 130°C; transfer line temperature, 140°C; vial equilibration time, 120 min. The chromatographic elution was carried out using HP-5MS column (30 m, 0.25 mm i.d. and 0.25 mm film thickness) (Chrom Tech., Apple Walley, MN, USA) with the following temperature program: 40°C, held for 5 min; 2°C/min up to 110°C, held for 1 min; 5°C/min up to 150°C, held for 1 min; 10°C/min up to 250°C, held for 20 min. The carrier gas was helium with a flow rate of 1 mL/min. The

injection port, MS source and MS quadrupole temperatures were set at 160°C, 230°C and 150°C respectively. The library of Wiley was used to identify the volatile compounds**.**

Analysis of 3-MCPD esters

The 3-MCPD ester contents were determined according to the DGF Standard Method C-VI 18 (10) (2009). The chromatographic separation was achieved using a capillary column (Restek Rxi-5 MS column, 30 m × 0.25 mm × 0.25 µm) and the injector was run in splitless mode. Carrier gas was helium with a flow rate of 1.18 mL/min. The oven temperature programme was set as follows: 80°C raised to 155°C with a heating rate of 5°C/min and then it was raised to 300°C with 60°C/min and held for 5 minutes. Temperature of ion source and interface in mass spectrometer was 200 and 280°C, respectively. Quantification of the results was carried out by monitoring characteristic ions at m/z 150 for 3-MCPD-d5 and m/z 147 for 3-MCPD.

Statistical analysis

Statistical analysis was carried out using SPSS 15 statistical software (SPSS Inc., Chicago, USA). Data were evaluated by one-way ANOVA procedure using the Duncan's multiple range test to see if there are any significant differences between refining steps. A *p* value of less than 0.05 was considered significant. All of the trials and analyses were duplicated.

RESULTS AND DISCUSSION

Table 1 shows the change in fatty acid composition of oils during refining. Main fatty acid was oleic acid (65.21-65.91%) for canola oil, whereas linoleic acid was found to be predominant for corn oil (56.44-57.74%). Besides, myristic (C14:0), pentadecanoic acid (C15:0), pentadecenoic acid (C15:1), palmitic (C16:0), palmitoleic (C16:1), linolenic (C18:3), arachidic (C20:0), myristic (C14:0), heptadecanoic (C17:0), heptadecenoic (C17:1), stearic (C18:0) and gadoleic (C20:1) acids were determined. The fatty acid composition of oils mainly covered the widely acknowledged limits for each type of oil determined in previous works (Karabulut et al., 2005; Mariod et al., 2006).

The change in sterol contents of oils during refining was given in Table 2. β-sitosterol, Δ-5-avenasterol, campesterol, brassicasterol, 24-methylene-cholesterol, campestanol, stigmasterol, Δ-7-campesterol, clerosterol, sitostanol, Δ-5-24-stigmastadienol, Δ-7-stigmastenol and Δ-7-avenasterol were identified in samples. Individual sterol contents and composition were mainly comparable to previous works determined for corn (Verleyen et al., 2002) and canola (Hamama et al., 2003) oils. Total sterols content of canola oil decreased from 8295.43 mg/kg to 7032.23 mg/kg as a result of refining process. A similar reduction (from 8912.02 mg/kg to 6752.06) because of refining was also observed in corn oil. The reduction ratio in total sterol was 15.22% and 42.57% in the same order. Neutralization step led to increases in both individual (campesterol, stigmasterol, beta-sitosterol, delta-5,24-stigmastadienol, delta-7-stigmastenol, delta-7-avenasterol) and total sterols contents of corn oil. In literature it was reported that during neutralization, large parts of the phytosterols (9-21%) are transferred by liquid-liquid partitioning to the soapstock (Gutfinger and Letan, 1974; Karaali, 1985). However in the study of Drira et al. (2018) it was stated that Δ-7-stigmastenol content of olive pomace oil increased during neutralization stage in accordance with the results of the current study.The major sterol was β-sitosterol and had a similar trend with total sterols. β-sitosterol comprised 51.56% of canola and 64.57% of corn oils on average. Campesterol was the other outstanding phytosterol covering about 35.89% of canola and 17.19% of corn oils. Canola oil was distinguished with its high brassicasterol content (8.92-10.16%). Stigmasterol contents of corn oil were higher with an average value of 5.77%. Total sterol content and individual sterol ratios were generally within the limits established for vegetable oils, set by Turkish Food Codex (2012) except for Δ-5-avenasterol which was found to be slightly lower than the threshold limit.

Table 1. Fatty acid composition of canola and oils throughout refining (%)

	C14:0	C15:0	C15:1	C 16:0	C16:1	C17:0	C17:1	C 18:0	C 18:1	C18:2	C18:3	C20:0	C20:1
Canola oil													
Crude	0.05^{B}	0.02^{A}	0.01^{A}	4.60^{B}	0.20^{B}	0.04^{A}	0.06^{A}	1.53^{AB}	65.21^{A}	20.04^{AB}	0.09^{B}	7.46^{B}	0.50^{AB}
Neutralized	0.04^{A}	0.03^{A}	0.02^{B}	4.23^{A}	0.19^{AB}	0.04^{A}	0.05^{A}	1.58^{C}	65.91^{B}	19.97^{A}	0.05^{AB}	7.26^{B}	0.55^{B}
Bleached	0.04^{AB}	0.02^{A}	0.01^{AB}	4.42^{B}	0.18^{A}	0.04^{A}	0.06^{A}	1.51^{A}	65.52^{AB}	20.22^{BC}	0.05^{AB}	7.32^{B}	0.48^{A}
Winterized	0.05^{AB}	0.01^{A}	0.02^{B}	4.46^{B}	0.19^{A}	0.04^{A}	0.05^{A}	1.56^{BC}	65.32^{A}	20.32^{C}	0.02^{A}	7.31^{B}	0.49^{AB}
Deodorized	0.05^{AB}	0.02^{A}	0.01^{AB}	4.53^{B}	0.19^{AB}	0.04^{A}	0.05^{A}	1.55^{ABC}	65.33^{A}	20.36^{C}	0.39^{C}	6.70^{A}	0.50^{AB}
Corn oil													
Crude	0.03^{a}	0.01^{a}	0.01^{a}	11.11^{b}	0.09^{a}	0.06^{ab}	0.03^{a}	1.89^{a}	28.77^{bc}	56.61^{bc}	0.07^{a}	0.89^{a}	0.36^{a}
Neutralized	0.03^{a}	0.01^{a}	0.01^{a}	11.31^{b}	0.11^{b}	0.07^{b}	0.02^{a}	1.98^{a}	27.58^{a}	57.41^{c}	0.09^{a}	0.91^{a}	0.34^{a}
Bleached	0.03^{a}	0.01^{a}	0.01^{a}	11.07^{b}	0.10^{ab}	0.07^{ab}	0.03^{a}	1.96^{a}	28.30^{b}	57.00^{bc}	0.07^{a}	0.89^{a}	0.36^{a}
Winterized	0.03^{a}	0.01^{a}	0.01^{a}	10.88^{ab}	0.12^{b}	0.07^{ab}	0.02^{a}	1.95^{a}	28.91^{c}	56.44^{a}	0.13^{a}	0.90^{a}	0.37^{a}
Deodorized	0.03^{a}	0.01^{a}	0.01^{a}	10.44^{a}	0.10^{ab}	0.06^{a}	0.03^{a}	1.97^{a}	30.92^{c}	57.74^{b}	0.11^{a}	0.81^{a}	0.43^{b}

Different superscript letters in the same column indicate significant differences (p<0.05) between different steps of refining for canola (A-C) and corn (a-c) oils.

Table 2. Sterol contents of canola and corn oils during refining (mg kg^{-1})

	Brassica-sterol	24-methylene-cholesterol	Campe-sterol	Campe-stanol	Stigma-sterol	Δ-7-Campe sterol	Clero-sterol	β-sitosterol
Canola oil								
Crude	842.74^{C}	2.32^{A}	3043.54^{B}	7.60^{A}	27.14^{A}	9.05^{A}	30.20^{C}	4123.66^{AB}
Neutralized	796.98^{BC}	1.33^{A}	2921.60^{B}	6.32^{A}	24.34^{A}	12.48^{A}	35.23^{C}	4065.82^{AB}
Bleached	726.82^{B}	4.09^{A}	2842.41^{B}	4.96^{A}	33.90^{A}	18.15^{A}	19.25^{B}	4217.21^{B}
Winterized	722.89^{B}	1.19^{A}	2801.03^{B}	1.00^{A}	21.46^{A}	17.94^{A}	1.81^{A}	4241.63^{B}
Deodorized	637.35^{A}	3.99^{A}	2538.36^{A}	1.97^{A}	24.30^{A}	12.08^{A}	16.18^{B}	3629.79^{A}
Corn oil								
Crude	7.27^{c}	6.02^{c}	1651.77^{b}	114.60^{e}	434.71^{a}	9.43^{b}	35.48^{a}	5090.18^{b}
Neutralized	1.36^{a}	-	2389.88^{d}	67.41^{b}	597.97^{b}	0.19^{a}	22.05^{a}	8302.79^{e}
Bleached	2.63^{b}	11.44^{e}	1715.68^{b}	73.69^{c}	446.36^{a}	2.41^{a}	31.70^{a}	5565.41^{c}
Winterized	9.27^{d}	5.89^{b}	1879.25^{c}	82.10^{a}	508.13^{a}	1.79^{a}	25.68^{a}	5520.82^{d}
Deodorized	17.32^{e}	7.46^{d}	1498.39^{a}	82.78^{d}	472.23^{a}	3.37^{a}	22.40^{a}	4281.63^{a}

	Sitostanol	Δ-5-avena-sterol	Δ-5,24 stigma - stadienol	Δ-7-stigma-stenol	Δ-7-avena-sterol	Total Sterols
Canola oil						
Crude	15.97^{A}	135.24^{A}	27.80^{A}	20.11^{A}	10.01^{A}	8295.43^{B}
Neutralized	3.69^{A}	122.67^{A}	21.55^{A}	19.87^{A}	11.80^{A}	8023.75^{B}
Bleached	65.85^{A}	58.62^{A}	39.98^{B}	19.28^{A}	6.31^{A}	8056.89^{B}
Winterized	5.47^{A}	109.63^{A}	45.65^{B}	16.17^{A}	6.57^{A}	7991.32^{B}
Deodorized	2.39^{A}	102.44^{A}	39.47^{B}	16.61^{A}	7.25^{A}	7032.23^{A}
Corn oil						
Crude	275.91^{d}	135.68^{b}	27.19^{a}	45.63^{a}	46.17^{d}	8912.02^{c}
Neutralized	124.37^{a}	95.64^{a}	41.51^{a}	56.34^{c}	58.78^{e}	11758.34^{d}
Bleached	177.06^{b}	101.82^{a}	47.18^{e}	44.81^{a}	37.57^{a}	8257.82^{b}
Winterized	176.14^{c}	75.73^{b}	48.12^{d}	52.25^{b}	44.31^{c}	8429.49^{c}
Deodorized	153.94^{c}	83.94^{a}	45.23^{c}	45.33^{e}	38.03^{e}	6752.06^{a}

Different superscript letters in the same column indicate significant differences (p<0.05) between different steps of refining for canola (A-C) and corn (a-e) oils.

Volatile compounds of oil samples were analyzed by gas chromatography coupled with mass spectrometry using static headspace extraction technique. Total peak areas of volatile compounds at different stages of refining for oils were given in Figure 1.

Canola oil was found to be poorer for volatile compounds, when compared to corn oil. Total volatile loss during refining was 86.81% and 84.50% for canola and corn oils respectively. Total volatiles decreased gradually for canola oil, however an increase was observed at bleaching step of corn oil. The increase in volatile components might be due to the decomposition of hydroperoxides into lower-molecular-weight compounds during bleaching step as was earlier indicated by Qizhi et al. (2008). Some selected volatiles determined comparatively in higher amounts for corn and canola oils was given in Table 3. Similar to total volatile content, individual volatiles had increments at bleaching step, and decreased after then in the case of corn oil. Pyrazine, 2,5-dimethyl-; furan-2-methyl; and 2-octyne were conspicuous peaks for corn oil; and nonanal was found to be in significant amounts for canola. After winterization stage there was a considerable loss of volatiles. It is well-known that the volatile loss during deodorization is due to the stripping effect of steam which lead to the removal of volatiles (Hoed et al., 2006). The same trend was observed within the current study.

The changes in the content of 3-MCPD esters of corn and canola oils during different steps of refining was shown in Figure 2. The content of 3-MPCD esters varied between 0.19 and 0.26 mg kg^{-1} for corn oil in accordance with previous results (Kuhlmann, 2011). The maximum concentration of ester bound 3-MCPD was detected during

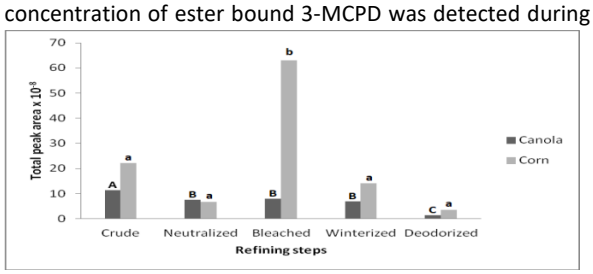

Figure 1. Change in total volatile contents of canola and corn oils during refining

Different superscript letters indicate significant differences (p<0.05) between different steps of refining for canola (A-C) and corn (a-e) oils.

Table 3. Selected volatile compounds of corn and canola oils during refining (GC-MS-HS peak area x10^{-6})

Selected volatiles	Crude	Neutralized	Bleached	Winterized	Deodorized
	Canola oil				
Heptanal	-	-	12.72	8.48	5.92
Trans-2-heptenal	-	-	-	-	22.68
Trans-2-*trans*-4-heptadienal	0.82	7.63	-	11.93	5.72
Octanal	7.92	3.71	-	10.54	4.35
Nonanal	12.79	10.80	28.98	25.05	16.52
	Corn oil				
2-furanmethanol	57.39	30.68	-	-	-
Pyrazine, 2,5-dimethyl-	918.22	28.09	-	-	-
Furan-2-methyl	130.29	48.86	134.61	45.91	-
1H-Pyrrole-2-carboxaldehyde, 5-methyl-	4.63	0.91	-	-	-
7-Oxabicyclo[4.1.0]heptane, 2-methylene-	-	-	51.16	-	-
2-Phenyl-2-butenal	13.98	11.70	-	-	-
2-Octyne	-	-	199.40	10.64	-
5-Methyl-2-phenyl-2-hexenal	2.75	2.83	4.81	1.62	-

deodorization step in accordance with the former works in literature (Pudel et al., 2011; Matthäus et al., 2011) which underline that deodorization was the most effective stage inducing the formation of 3-MCPD esters for different oils.

The concentration of 3-MCPD esters were generally higher in corn oils when compared to canola oils except the last step of refining, namely deodorization. In literature, it was highlighted that different oils from various origins have different capabilities to form 3-MCPD esters. Matthäus et al. (2011) reported that rapeseed oil showed amounts of 3-MCPD esters and related compounds below 1 mg/kg after heat treatment, while corn oil contained much higher amounts of the esters in accordance with the presented results. The precursors for the formation of 3-MCPD esters were defined as monoacylglycerols (MAGs), diacylglycerols (DAGs) and phospholipids (Hamlet et al., 2004a; Hamlet et al., 2004b). Moreover Calta et al. (2004) and Velíšek et al. (2003) reported that the formation of free 3-MCPD strongly depends on temperature and the amount of lipids, salt, water and glycerol. In addition to triglycerides (TAGs) fats and oils comprise of different amounts of free fatty acids, MAGs and DAGs depending on the origin of the raw material. All of these compositional parameters were attributed as a possible source of the formation of 3-MCPD esters (Matthäus et al., 2011). The unrefined canola oil contained 0.20 mg kg^{-1} 3-MCPD esters and the concentration increased to 0.48 mg kg^{-1} after deodorization. The results were in accordance with former works (Kuhlmann, 2011).

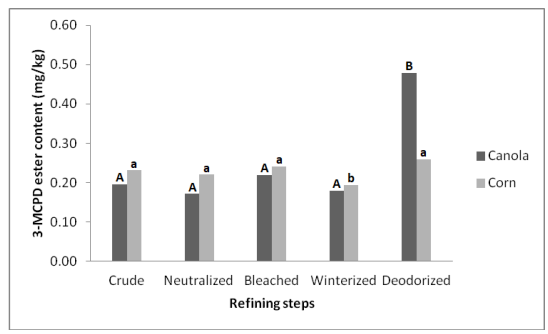

Figure 2. Changes in 3-MCPD ester contents of corn and canola oils during refining

Different superscript letters indicate significant differences (p<0.05) between different steps of refining for canola (A-C) and corn (a-e) oils.

CONCLUSION

The results of the study clearly showed that individual refining stages were directly influential on the composition of canola and corn oils. Total sterol content of canola and corn oils were between 8295.43-7032.23 mg kg^{-1} and 11758.34-6752.06 mg kg^{-1} respectively. The reduction ratio in total sterol was 15.22% and 42.57% in the same order. Canola oil was found to be poorer for volatile compounds, when compared to corn oil. Total volatile loss during refining was 86.81% and 84.50% for canola and corn oils respectively. Total volatiles of canola oil decreased gradually during refining, however corn oil had significant increases at bleaching step. The maximum amount of 3-MCPD esters was detected during deodorization step in accordance with a number of previous studies. The concentration of 3-MCPD esters were generally higher in corn oils when compared to canola oils except deodorization stage.

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REFERENCES

Alpaslan M, Tepe S, Simsek O (2001) Effect of Refining Processes on the Total and individual Tocopherol Content in Sunflower Oil. International Journal of Food Science and Technology 36: 737-739.

AOCS (2003) Official Methods and Recommended Practices of the American Oil Chemists' Society AOCS Press, Champaign.

Bachari-Saleh Z, Ezzatpanah H, Aminafshar M, Safafar H (2013) The Effect of Refining Process on the Conjugated Dienes in Soybean Oil. Journal of Agricultural Science and Technology 15: 1185-1193.

Bortolomeazzi R, Cordaro F, Pizzale L, Conte LS (2003) Presence of Phytosterol Oxides in Crude Vegetable Oils and Their Fate During Refining. Journal of Agricultural and Food Chemistry 51: 2394-2401.

Calta P, Velíšek J, Doležal M, Hasnip S, Crews C, Réblová Z (2004) Formation of 3-Chloropropane-1,2-Diol in Systems Simulating Processed Foods. European Food Research and Technology 218: 501-506.

Craft BD, Nagy K, Sandoz L, Destaillats F (2012) Factors Impacting the Formation of Monochloropropanediol (MCPD) Fatty Acid Diesters During Palm (*Elaeis guineensis*) Oil Production. Food Additives and Contaminants: Part A 29: 354-361.

DGF (2009) German Standard Methods for the Analysis of Fats and other Lipids: C-VI 18 (10) A & B, Ester-Bound 3-Chloropropane-1,2-Diol (3-MCPD Esters) and Glycidol (Glycidyl Esters): Determination in Fats and Oils by GC-MS, WVG. 2009.

Drira M, Jabeur H, Marrakchi F, Bouaziz M (2018) Delta-7-stigmastenol: Quantification and Isomeric Formation During Chemical Refining of Olive Pomace Oil and Optimization of the Neutralization Step. European Food Research and Technology 244: 2231-2241.

El-Mallah MH, El-Shami SM, Hassanien MMM, Abdel-Razek AG (2011) Effect of Chemical Refining Steps on the Minor and Major Components of Cottonseed Oil. Agriculture and Biology Journal of North America 2: 341-349.

Farhoosh R, Einafshar S, Sharayei P (2009) The Effect of Commercial Refining Steps on the Rancidity Measures of Soybean and Canola Oils. Food Chemistry 115: 933–938.

Ferrari RA, Schulte E, Esteves W, Bruhl L, Mukherjee KD (1996) Minor Constituents of Vegetable Oils during Industrial Processing. Journal of the American Oil Chemists' Society 73: 587–592.

Garcia A, Ruiz-Méndez MV, Romero C, Brenes M (2006) Effect of Refining on the Phenolic Composition of Crude Olive Oils. Journal of the American Oil Chemists' Society 83: 159-164.

Gutfinger T, Letan A (1974) Studies of Unsaponifiables in Several Vegetable Oils. Lipids 9: 658-663.

Hamama AA, Bhardwaj HL, Starner DE (2003) Genotype and Growing Location Effects on Phytosterols in Canola Oil. Journal of the American Oil Chemists' Society 80: 1121–1126.

Hamlet CG, Sadd PA, Gray DA (2004a) Generation of Monochloropropanediols (MCPDs) in Model Dough Systems. 1. Leavened Doughs. Journal of Agricultural and Food Chemistry 52: 2059-2066.

Hamlet CG, Sadd PA, Gray DA (2004b) Generation of Monochloropropanediols (MCPDs) in Model Dough Systems. 2. Unleavened Doughs. Journal of Agricultural and Food Chemistry 52: 2067-2072.

Hoed VV, Depaemelaere G, Ayala JV, Santiwattana P, Verhé R, Greyt WD (2006) Influence of Chemical Refining on the Major and Minor Components of Rice Bran Oil. Journal of the American Oil Chemists' Society 83: 315–321.

IUPAC (1987) Standard Methods for Analysis of Oils, Fats and Derivates, International Union of Pure and Applied Chemistry, 7th ed. IUPAC Method 2.301, Blackwell Scientific Publications.

Johansson A, Hoffmann I (1979) The Effect of Processing on the Content and Composition of Free Sterols And Sterol Esters in Soybean Oil. Journal of the American Oil Chemists' Society 56: 886–889.

Jung MY, Yoon SH, Min DB (1989) Effect of Processing Steps on the Contents of Minor Compounds and of Soybean Oil. Journal of the American Oil Chemists' Society 66: 118–120.

Karaali, A (1985) The Effects of Refining on the Chemical Composition of Turkish Sunflower Seed Oil. Fette, Seifen, Anstrichmittel 87: 112-117.

Karabulut I, Topcu A, Yorulmaz A, Tekin A, Ozay DS (2005) Effects of the Industrial Refining Process on Some Properties of Hazelnut Oil. European Journal of Lipid Science and Technology 107: 476–480.

Kraljić K, Škevin D, Barišić L, Kovačević M, Obranović M, Jurčević I (2015) Changes in 4-Vinylsyringol and Other Phenolics During Rapeseed Oil Refining. Food Chemistry 187: 236–242.

Krishna AG, Khatoon GS, Shiela PM, Sarmandal CV, Indira TN, Mishra A (2001) Effect of Refining of Crude Rice Bran Oil on the Retention of Oryzanol in the Refined Oil. Journal of the American Oil Chemists' Society 78: 127–131.

Kuhlmann J (2011) Determination of Bound 2, 3-Epoxy-1-Propanol (Glycidol) and Bound Monochloropropanediol (MCPD) in Refined Oils. European Journal of Lipid Science and Technology 113: 335-344.

Qizhi L, Yonghui H, Haiyan Z, Bedgood Jr DR, Prenzler PD, Robards K (2008) The Quality and Volatile-Profile Changes of Camellia Oil (Camellia Oleifera Abel) Following Bleaching. European Journal of Lipid Science and Technology 110: 768-775.

Mariod A, Matthäus B, Eichner K, Hussein IH (2006) Effects of Processing on the Quality and Stability of Three Unconventional Sudanese Oils. European Journal of Lipid Science and Technology 108: 298–308.

Matthäus B, Pudel F, Fehling P, Vosmann K, Freudenstein A (2011) Strategies for the Reduction of 3-MCPD Esters and Related Compounds in Vegetable Oils. European Journal of Lipid Science and Technology 113: 380-386.

Naz S, Sherazi STH, Talpur FN (2011) Changes of Total Oil Processing. Journal of the American Oil Chemists' Society 88: 127–132.

Ortega-García J, Gámez-Meza N, Noriega-Rodriguez JA, Dennis-Quiñonez O, García-Galindo HS, Angulo-Guerrero JO, Medina-Juárez, LA (2006) Refining of High Oleic Safflower Oil: Effect on the Sterols and Tocopherols Content. European Food Research and Technology 223: 775–779.

Petrauskaitè V, Greyt WFD, Kellens MJ (2000) Physical Refining of Coconut Oil: Effect of Crude Oil Quality and Deodorization Conditions on Neutral Oil Loss. Journal of the American Oil Chemists' Society 77: 581–586.

Pudel F, Benecke P, Fehling P, Freudenstein A, Matthäus B, Schwaf A (2011) On the Necessity of Edible Oil Refining and Possible Sources of 3-MCPD and Glycidyl Esters. European Journal of Lipid Science and Technology 113: 368-373.

Sánchez-Machado DI, López-Cervantes J, Núñez-Gastélum JA, Mora-López GS, López-Hernández J, Paseiro-Losada P (2015) Effect of the Refining Process on Moringa Oleifera Seed Oil Quality. Food Chemistry 187: 53–57.

Tasan M, Demirci, M (2003) *Trans* FA in Sunflower Oil at Different Steps of Refining. Journal of the American Oil Chemists' Society 80: 825– 828.

Tasan M, Demirci M (2005) Total and Individual Tocopherol Contents of Sunflower Oil at Different Steps of Refining. European Food Research and Technology 220: 251–254.

Teixeira VH, Casal S, Oliveira MBPP (2007) PAHs Content in Sunflower, Soybean and Virgin Olive Oils: Evaluation Tocopherol and Tocopherol Species during Sunflower in Commercial Samples and During Refining Process. Food Chemisty 104: 106–112.

Tubaileh RM, Garrido-Fernández A, Ruiz-Mendez MV, León-Camacho M, Graciani-Constante E (2002) Effects of Physical Refining on Content of Waxes and Fatty Alcohols of Refined Olive Oil. Journal of the American Oil Chemists' Society 79: 101–104.

Turkish Food Codex (2012) Communique on Edible Vegetable Oils Called by Plant Names. The Official Gazette of Republic of Turkey, Number 28262, 12 April 2012.

Velíšek J, Calta P, Crews C, Hasnip S, Doležal M. (2003). 3-Chloropropane-1, 2-Diol in Models Simulating Processed Foods: Precursors and Agents Causing Its Decomposition. Czech Journal of Food Sciences 21: 153.

Verleyen T, Sosinska U, Ioannidou S, Verhe R, Dewettinck K, Huyghebaert A, Greyt WD (2002) Influence of the Vegetable Oil Refining Process on Free and Esterified Sterols. Journal of the American Oil Chemists' Society 79: 947–953.

Wang T, Johnson LA (2001) Refining High-Free Fatty Acid Wheat Germ Oil. Journal of the American Oil Chemists' Society 78: 71–76.

Wei J, Chen L, Qiu X, Hu W, Sun H, Chen X, Bai Y, Gu X, Wang C, Chen H, Hu R, Zhang H, Shen G. (2015). Optimizing Refining Temperatures to Reduce the Loss of Essential Fatty Acids and Bioactive Compounds in Tea Seed Oil. Food and Bioproducts Processing 94: 136-146.