Acta Alimentaria, Vol. 33 (1), pp. 7–18 (2004)

THE EFFECT OF PROCESSING CONDITIONS ON THE NONTRIACYLGLYCEROL CONSTITUENTS OF SUNFLOWER OIL

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(Received: 15 July 2002; accepted: 27 March 2003)

In this study samples of non-refined sunflower oils, obtained in industrial and laboratory scale by cold and hot pressing and hexane extraction, as well as sunflower oils from single refining steps were investigated. The content and composition of carotenoids, sterols, and the content of chlorophylls as well as oxidative stability were investigated. To obtain the data about the acidity and oxidative status of the oil samples, basic quality analyses of free fatty acid content (FFA), peroxide value (PV) and spectrophotometric analyses in UV area (K232, K270 and ΔK) were used.

The results showed that the predominating carotenoid in sunflower oil is lutein, and that the total amount of carotenoids during refining process was reduced to about 15% of the initial amount. The major sterol in sunflower oil (about 70%), as well as in other vegetable oils, was β-sitosterol. The other important sterols in sunflower oil were Δ^7-stigmasterol, stigmasterol, campesterol, Δ^5-avenasterol and Δ^7-avenasterol. The composition of sterols in non-refined and refined oils was more or less the same, while the content of sterols during refining process decreased by 22%. Among all analysed sunflower oils, the laboratory extracted oil had the best oxidative stability (e.g. the longest induction period, according to Rancimat method), while cold and hot pressed oils were less stable than the fully refined one.

Keywords: non-refined sunflower oil, refining, nontriacylglicerols

Edible fats and oils consist mainly of triacylglycerols and the physical and chemical characteristics of lipids are determined primarily by their fatty acid composition. The triacylglycerols generally co-exist with nontriacylglycerols or minor components, and these are represented mainly by the unsaponifiable matter. Most oils contain 1–2% unsaponifiable matter, depending on the type of oil as well as on processing conditions. The minor components are primarily composed of phospholipids, tocopherols, tocotrienols, flavonoids, carotenoids, chlorophylls and sterols. The composition of the minor components provides highly specific information about the quality and identity of oils. Oxidative stability and deterioration of oils depend on fatty acid (FA) composition and concentration of minor compounds with antioxidant or prooxidant characteristics. Oxidation of oils not only affects their flavour characteristics, but also influences their wholesomeness and nutritional value (SHAHIDI & SHUKLA, 1996). The sterol fraction

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has been analysed in order to determine the identity, sometimes also the quality of oil or fat, and to detect the addition of cheap oils to more expensive oils (GROB & BRONZ, 1994).

Many of the nontriacylglycerol compounds are also indispensable for maintaining correct metabolism. Therefore, it is very important to preserve these components as much as is possible during oil processing and avoid over processing.

Sunflower (*Helianthus annuus* L.) is one of four major annual oilseed crops produced in the world. Most processing plants extract sunflower oil by pre-pressing followed by hexane extraction. The solvent extraction process increases yield of the obtained oil, but the oil contains the impurities which must be removed, which means that the extracted oils have to be refined. Refining of oils comprises several physical and chemical processes which aim at eliminating the unnecessary substances and other contaminants (pesticides, heavy metals), but during refining nontryacilglycerol substances, such as antioxidants, vitamins, provitamins, are also being removed (DAVIDSON et al., 1996).

Today many consumers avoid buying edible oils produced by solvent extraction and refining. They prefer native edible oils produced exclusively by pressing or other physical procedures under conditions which do not lead to deterioration of the oil. Among these oils olive oil has got the largest market share, but other kinds of cold pressed oils (CPO) such as sunflower, maize, pumpkin seed and recently also rapeseed oils are becoming more and more important on the market. These new products usually do not have the same guarantees of quality and authenticity as extra virgin olive oil.

CPOs (Cold Pressed Oils) provide typical flavours and tastes in contrast to tasteless and odourless refined edible oils. The shelf life of CPOs compared to refined oils is often shorter, because some of these oils contain prooxidative substances such as chlorophylls and hydroperoxides. On the other hand, valuable ingredients in CPOs do not degrade when pressing is done at low temperatures (≤50 °C) (DE PANFILIS et al., 1998). According to the findings of WILLNER and co-workers (1997), warm pressing of the press cake results in twice as high a concentration of tocopherols in the oil as cold pressing of the whole seed.

Nontriacylglycerol compounds should not be excluded from quality control analysis of oils and fats, because they provide specific characteristics and are important indicators of quality and authenticity of product. The content and share of these compounds in oil depend on oil type as well as on the conditions of the manufacture and subsequent refining process.

Each processing step in the refining of edible oils is designed to perform a specific function for removing certain minor components from the oil. Knowledge of composition and content of nontriacylglycerol compounds in oil enables selecting of optimal conditions during the oil manufacture and oil refining process which helps preserve nutrients and biological properties of all ingredients and eliminate undesirable compounds and impurities.

The aim of the present study was to investigate the effect of processing conditions (cold and hot pressing, solvent extraction), as well as refining steps on the nontriacylglycerol compounds of sunflower oil, and their influence on the quality and oxidative stability of sunflower oil.

1. Materials and methods

Sunflower oil samples obtained in industrial and laboratory scale were used for the investigations.

Industrial oil samples were produced under usual industrial conditions and obtained from a local oil factory: industrial crude oil (CO) (obtained by pressing of seed and subsequent hexane extraction of oilcake was water degummed), alkali refined oil (ARO), bleached oil (BO) and deodorized oil (DO). Industrial samples of cold pressed oil (CPO) were purchased from a local market.

Laboratory oil samples were obtained by pressing or hexane extraction of sunflower seed of domestic origin, grown in 2000. The oil and moisture content of seeds used in experiments was 48.5% and 9.4%, respectively. Processes were performed using whole (not dehulled) seed and involved grinding, cooking and pressing or extraction. Oil was pressed from seeds with a Komet screw press (Model CA/59; IBG Monforts & Reiners, Rheydt, Germany) with compression screw R8 and screw speed of 45 r.p.m. Pressed oils were vacuum filtered over a Büchner funnel and stored in brown bottles at 4 °C until analysis.

Hot pressed oil (LHPO): Seeds were ground in a coffee mill, cooked at 100 °C for 30 min, and then pressed. The screw press was heated via an electrical resistance heating ring attached around the press head. The barrel temperature was maintained at 120 °C during pressing.

Cold pressed oil (LCPO): Oil was extracted from the ground seeds by simple pressing without cooking and press heating, however, temperature in the head of the press was increased during pressing to about 70 °C.

Extracted oil (LEO): Seeds were ground and extracted with hexane in a Soxhlet apparatus, for 8 h and hexane was removed from oil by a rotary evaporator.

Standards (cholestanol, cholesterol, sitosterol, α-tocopherol) and specific chemical reagents for sterol determination were supplied by Sigma Chemical Co. (St. Louis, MO). Other chemicals were of analytical grade from "Merck" and used without further purification.

- International ISO methods were used to determine free fatty acids (FFA) (ISO, 1996), peroxide value (PV) (ISO, 1977), specific absorbances (K_λ) in the ultraviolet (ISO, 1989).
- A.O.C.S. method (1993) was used to determine chlorophyll content in oil samples.
- Carotenoid pigments were isolated from the unsaponifiable matter of oil samples using an Al_2O_3 column. Identification and amount of each fraction from the column was done and determined on the basis of absorption spectra (D.G.F., 1975).

– All spectrometric measurements were performed on a Helios β UV-visible spectrometer (ATI Unicam).
– The sterol composition of the oils was determined according to the relevant ISO standard (1999). The sterol fraction was analysed by ATI Unicam 610 GC, with a split injector and FID detector. Capillary column was an SPB-5 (15 m ×0.32×0.25 μm). Helium was used as a carrier gas at a flow rate 2.8 ml·min^{-1}. The temperature regime was as follows: oven 260 °C, injector 280 °C, detector 290 °C; split ratio was 1:10 and the amount injected 0.5–1.0 μl. Sterols were quantified using cholestanol as internal standard. Chromatography software (Unicam 4880 chromatography data system) was employed for data collection.
– The stability to oxidation was determined by the 679 Rancimat (Metrohm Ltd. Herisau, Switzerland) at 100 °C (HADORN & ZÜRCHER, 1974).
– Thin layer chromatography of unsaponifiable matter of oil samples was made on Silica gel 60 plates (0.25 mm "Merck"). Solvent system of hexane-diethyl-ether (65:35) was used for separation (ISO, 1999). The plates were sprayed with α, α' dipyridil-ferrum (III) chloratum, and anisaldehyde reagent for the visualisation of the lipid spots (STAHL, 1967).

Data are expressed as mean values of duplicate analyses of three replicates. The average and standard deviation were calculated and analysis of variance and the LSD method was used for the evaluation of the data (MONTGOMERY, 1984).

2. Results

2.1. Main quality parameters and oxidative stability

The main quality parameters (FFA, PV, K_λ) and oxidative stability of different refined and non-refined sunflower oils used in this study are shown in Table 1.

Table 1. Free fatty acids, peroxide value and specific absorbances of sunflower oils with different processing conditions in UV[b]

Oil samples[a]	FFA (% oleic)	Peroxide value (mmol O_2 kg^{-1})	Specific absorbances		ΔK	Stability (h)
			K_{232}	K_{270}		
CO	1.60±0.26^{D}	6.20±0.34^{E}	2.974±0.09^{B,C}	0.323±0.02^{C,D}	0.016	7.8±0.31
ARO	0.06±0.01^{A}	7.95±0.36^{F}	3.004±0.02^{C}	0.307±0.01^{C}	0.020	8.2±0.15
BO	0.06±0.01^{A}	5.23±0.47^{D}	3.070±0.04^{C}	1.268±0.03^{E}	0.167	8.1±0.21
DO	0.03±0.01^{A}	0.05±0.03^{A}	3.474±0.07^{D}	1.664±0.05^{F}	0.223	9.8±0.12
CPO	1.07±0.23^{C}	4.28±0.43^{C}	2.773±0.07^{A,B}	0.243±0.03^{B}	0.013	7.5±0.20
LCPO	0.86±0.23^{C}	1.28±0.22^{B}	2.699±0.09^{A}	0.191±0.02^{A}	0.007	7.5±0.26
LHPO	0.91±0.17^{C}	1.33±0.11^{B}	3.013±0.02^{C}	0.356±0.01^{D}	0.016	8.4±0.15
LEO	0.50±0.09^{B}	1.13±0.09^{B}	3.029±0.07^{C}	0.332±0.02^{C,D}	0.032	13.9±0.25

[a] CO: crude oil; ARO: alkali-refined; BO: bleached; DO: deodorized; CPO: cold pressed in factory; LCPO: cold pressed in laboratory; LHPO: hot pressed in laboratory; LEO: extracted in laboratory.
[b] Means ± standard deviation of 3 replicates. Means within columns with different capital letters (A–F) are significantly different ($P<0.05$).

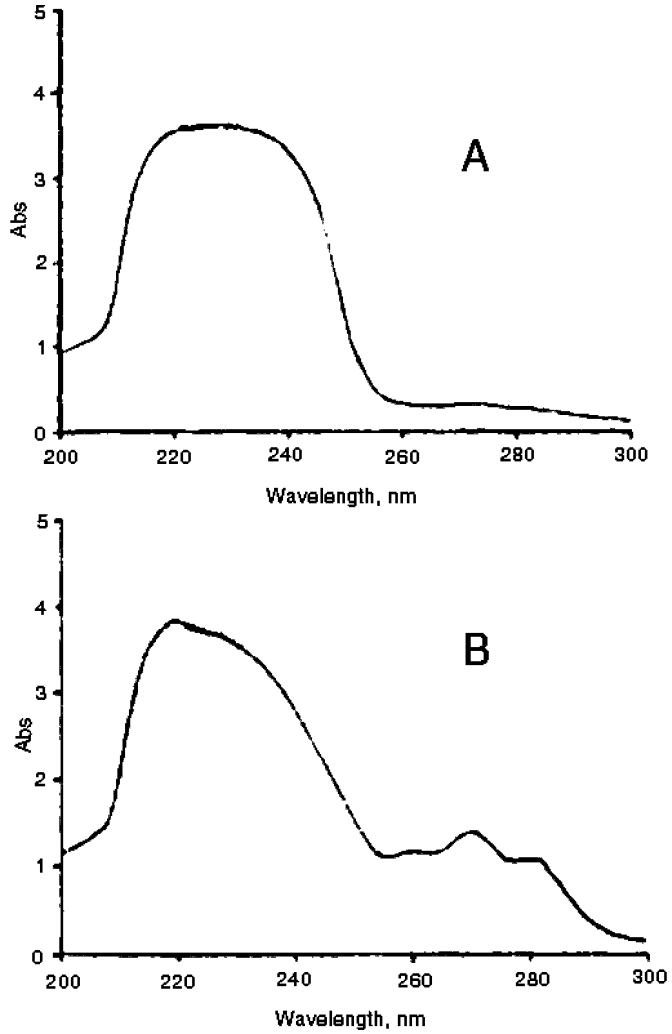

Fig. 1. Ultraviolet spectra (UV) of crude (A) and deodorized (B) sunflower oil

Data in Table 1 show that CO had the highest and DO the lowest FFA shares, which were to be expected (1.60 and 0.06%, respectively). All non-refined oils had FFA below the limit (2%) specified in regulations valid in Croatia for these oils (PRAVILNIK, 1999).

Peroxide value (PV) is a measure of the amount of peroxides formed in fats and oils through oxidation and autoxidation processes. The results in Table 1 indicate that

alkali refined oil had the highest PV value. This may be due to the heat treatment to which the oils were exposed. The bleaching and deodorization process decreased PV, because peroxides are also adsorbed to the bleaching agent and the peroxides' decomposition products (aldehydes and ketones) are removed during deodorization.

Oils, containing unsaturated fatty acids, are oxidized to conjugated diene and triene systems that can be measured by ultraviolet absorption at 232 and 270 nm. The absorbance at 232 nm is an indicator of the formation of conjugated dienes, which also measures the degree of primary oxidation. Absorbance at 270 nm measures conjugated trienes, secondary oxidative products in oil. Results in Table 1 show that the values for absorbance at 232 nm were lower for CPO and LCPO (2.69) and CPL (2.74) than for other oils which were about 3.0 except DO, which was 3.41. The absorbance values at 270 nm were higher for deodorized and bleached oils (1.66 and 1.26, respectively) than for other oils, which were between 0.19 (for LCPO) and 0.35 (for LHPO). Data (Table 1 and Fig. 1) show that conjugated products are also formed during bleaching and deodorization of oils.

According to European Community (EC) regulations (1991), maximal absorbance at 270 nm for virgin olive oil is 0.25 and $\Delta K \leq 0.01$, but for other cold pressed oils there are no regulations. Olive oil with the specific absorbance higher than 0.25 at 270 nm is considered as virgin oil, provided that after passage trough a column with alumina the absorbance is lower than 0.11. Absorbance higher than 0.11 suggests the presence of refined oil. Some authors (OŠTRIĆ-MATIJAŠEVIĆ & TURKULOV, 1980) reported that for good quality non-refined sunflower oil absorbance at 270 nm must be below 0.5.

The oxidative stability of refined and non-refined sunflower oils used in this study are presented as induction time in hours.

It is evident (Table 1) that laboratory extracted oil (LEO) had the highest oxidative stability. By comparing refined deodorized oil and non-refined oils, it can be seen that deodorized oil had a higher oxidative stability than all non-refined oils. Differences in oxidative stability may be due to initial peroxide values, which were lower in LEO and DO than in other oil samples. The peroxides function as catalysts for oil oxidation.

2.2. Pigments

Carotenoids and chlorophylls are the two most common pigments present in most vegetable oils. In edible oils, they can influence lipid oxidation. Chlorophyll is a common sensitizer that acts as a promoter of photo-oxidation in oil systems. Carotenoids act as antioxidants against lipid peroxidation by quenching singlet oxigen and trapping free peroxy radicals (ANGUELOVA & WARTHESEN, 2000).

In the conventional refining process, the pigments are removed at various steps. The bleaching operation employing a clay product is an adsorption process that removes colour compounds, and during deodorization the thermally degradable carotenoids are also removed.

Chlorophyll and carotenoid content of sunflower oils with different processing conditions is shown in Table 2.

Table 2. Chlorophyll and carotenoid content and carotenoid composition of sunflower oils with different processing conditions[b]

Oil samples[a]	Chlorophyll (mg kg^{-1})	Carotenoid			
		total (mg kg^{-1})	composition (% of the total)		
			carotene	cryptoxanthin	lutein + zeaxanthin
CO	0.63±0.02^{E}	2.77±0.08^{F}	12.7±0.50^{D}	10.9±0.21^{C}	76.4±0.40^{B}
ARO	0.48±0.03^{D}	2.57±0.04^{E}	13.1±0.25^{D}	9.8±0.40^{B}	77.1±0.40^{B}
BO	0.06±0.01^{A}	0.65±0.05^{B}	34.1±0.20^{E}	14.6±0.30^{E}	51.3±0.20^{A}
DO	0.04±0.01^{A}	0.42±0.09^{A}	4.9±0.20^{A}	43.0±0.40^{F}	52.1±0.46^{A}
CPO	0.36±0.04^{C}	1.26±0.07^{D}	12.5±0.30^{D}	10.7±0.20^{C}	76.8±0.30^{B}
LCPO	0.02±0.01^{A}	1.15±0.06^{C}	8.9±0.40^{B}	13.9±0.45^{D}	77.2±0.30^{B}
LHPO	0.32±0.02^{C}	1.31±0.06^{D}	9.9±0.46^{C}	13.6±0.36^{D}	76.5±0.36^{B}
LEO	0.23±0.06^{B}	1.33±0.05^{D}	10.5±0.64^{C}	8.6±0.30^{A}	80.9±0.31^{C}

[a] For sample codes see Table 1.

[b] Means ± standard deviation of 3 replicates. Means within columns with different capital letters (A–F) are significantly different ($P<0.05$).

The results show that sunflower oil had a low level of chlorophyll pigments. Crude oil (CO) had the most chlorophylls (0.63 mg kg^{-1}), which were removed during bleaching. Industrial cold pressed oil (CPO) had higher chlorophyll content than laboratory cold pressed (LCPO) and extracted oil (LEO), but the same as laboratory hot pressed oil (LHPO).

In crude sunflower oil the amount of total carotenoids was 2.86 mg kg^{-1}, and in all other non-refined oils about 1.2 mg kg^{-1}.

During refining process, carotenoids are somewhat removed by alkali refining, and the maximal reduction (77%) occurs during bleaching. In the subsequent deodorization step, carotenoids are removed, amounting to total reduction of 85%.

All these oils (except bleached oil) contain mainly xanthophylls (predominantly dihydroxy carotenoids). During bleaching more xanthophylls were removed than carotenoids, however, the remaining carotenoids were then removed during deodorization.

The composition of major carotenoids in non-refined oils was 76 to 81% dihydroxy carotenoids (mostly lutein), 8.6 to 14% cryptoxanthin and 8.9 to 12.7% carotene (Table 2).

These results show that xanthophylls are the major carotenoids in sunflower oil, as well as in soybean, rapeseed, sesame and other seed oils (VOGEL, 1977). MONMA and co-workers (1994) suggested that β-carotene, a photoprotective antioxidant in photosynthetic tissue, decreased more rapidly than other pigments during the process of seed maturation. Therefore, xanthophylls are the major carotenoids in the oils extracted from soybean and rapeseed.

Since most of the carotenoids are lost during oil bleaching and at high temperatures during deodorization, some β-carotene may be added to edible oils in order to extend their shelf life during storage under supermarket conditions to inhibit photosensitised oxidation (SHAHIDI & SHUKLA, 1996).

The antioxidant effect of β-carotene against lipid peroxidation is accompanied by degradation of the pigment and loss of colour. γ-Tocopherol was reported to protect the degradation of lutein and lycopene during oxidation of triacylglycerols. On the other hand, very low levels of carotenoids prolonged the lifetime of α-tocopherol during photooxidation of membrane phospholipids (ANGUELOVA & WARTHESEN, 2000).

The absorption spectra in the visible range of all oil samples are presented in Fig. 2.

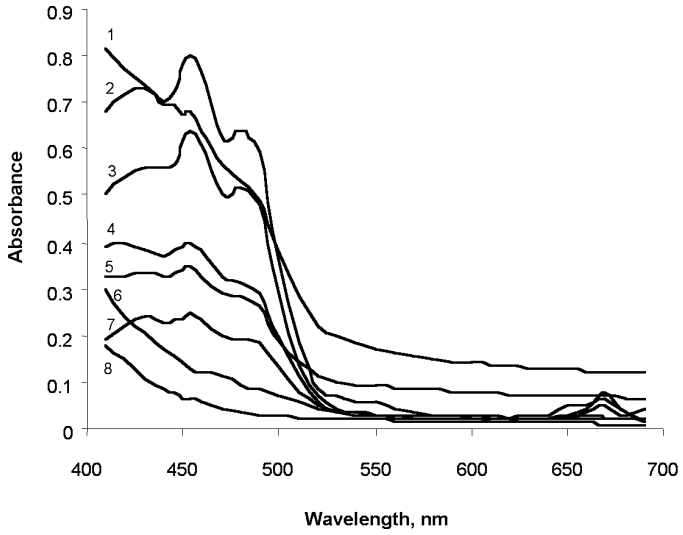

Fig. 2. Absorption spectra in the range of 400–700 nm of sunflower oils with different processing conditions. CO(2): crude oil; ARO(3): Alkali refined; BO(6): bleached; DO(8): deodorized; CPO(4): cold pressed in factory; LCPO(7): cold pressed in laboratory; LHPO(1): hot pressed in laboratory; LEO(5): extracted in laboratory

The curves show that neither BO and DO have maximum in the range 440–480 nm nor in range 667–670 nm. Only CO, ARO and CPO have maximum at 670 nm.

2.3. Sterols

Sterols comprise a major portion of the unsaponifiable matter in most vegetable oils. Many researchers have used the sterol pattern of oils in order to characterize and fingerprint them or to detect adulteration. Refining causes dehydration of most of the sterols and elimination of the acid group of sterol esters. The analysis of stigmastadiene, the degradation product of β-sitosterol, which is the major sterol in vegetable oils, was suggested for the distinction between refined oil and extra virgin olive oil. Normally, refined oils typically contain 2–20 mg kg^{-1} of stigmastadiene, the main degradation product of sitosterol, whereas all really unrefined oils contained less than 0.02 mg kg^{-1}.

Table 3 shows the sterols in sunflower oils with different processing conditions.

Table 3. Composition and content of sterols in sunflower oil with different processing conditions[b]

Oil samples[a]	Total (mg kg^{-1})	Composition (% of the total)					
		campe-sterol	stigma-sterol	β-sitosterol	Δ7-stigma-sterol	Δ7-avena-sterol	Δ5-avena-sterol
CO	3750±224.0^{F}	9.0±0.80	6.6±0.40	71.7±0.61	9.2±0.26	2.7±0.25	1.1±0.24
ARO	3533±71.8^{E}	9.1±0.40	6.8±0.30	72.3±0.69	9.1±0.80	2.4±0.46	–
BO	3034±64.3^{A,B}	10.1±0.61	7.2±0.52	70.7±0.55	9.5±0.31	2.9±0.70	–
DO	2965±93.2^{A}	10.5±0.80	7.1±0.25	69.9±1.21	9.8±0.45	2.8±0.40	–
CPO	3208±108.2^{B,C}	9.3±0.65	5.7±0.50	70.7±1.11	9.9±0.45	3.7±0.53	1.0±0.18
LCPO	3370±47.5^{C,D,E}	8.6±0.61	5.7±0.53	72.3±0.59	9.9±0.65	3.5±0.36	–
LHPO	3429±90.5^{D,E}	8.3±0.65	5.3±0.20	71.3±0.51	10.4±0.62	3.8±0.26	1.2±0.30
LEO	3278±130.6^{C,D}	8.2±0.40	5.9±0.62	71.7±0.35	10.2±0.36	3.3±0.26	0.8±0.06

[a] For sample codes see Table 1.
[b] Means ± standard deviation of 3 replicates. Means within columns with different capital letters (A–F) are significantly different ($P<0.05$).

The data show that CO has the highest level of sterols (3750 mg kg^{-1}), and LEO has the lowest (2965 mg kg^{-1}). The highest amount of sterols was removed during bleaching (about 19%). Non-refined oils have between 3208 mg kg^{-1} (LCPO) and 3430 mg kg^{-1} (LHPO). The composition of sterols is not very different and β-sitosterol is the major sterol in all samples (about 70%). Stigmastadiene was not analysed in these oil samples.

Some investigations suggest that catalysis of sterol degradation is highly important and that it strongly depends on bleaching temperature and on the type and amount of earth involved. The formation of degradation product by deodoration starts being noticeable above 180 °C only. Oilseeds may be heated prior to pressing in order to inactivate enzymes and to improve the yield. The effect on the integrity of the sterols was tested by heating of sunflower seeds and walnuts. After heating for 1 h at 150 °C and 180 °C no stigmastadiene was detected. This not only indicates that the presence of degradation products is not a result of heating during oil manufacture, but also that this method is not suitable to distinguish oils pressed at low or high temperatures (GROB & BRONZ, 1994).

2.4. Thin layer chromatography

Qualitative composition of unsaponifiable matter of sunflower oils was performed by TLC.

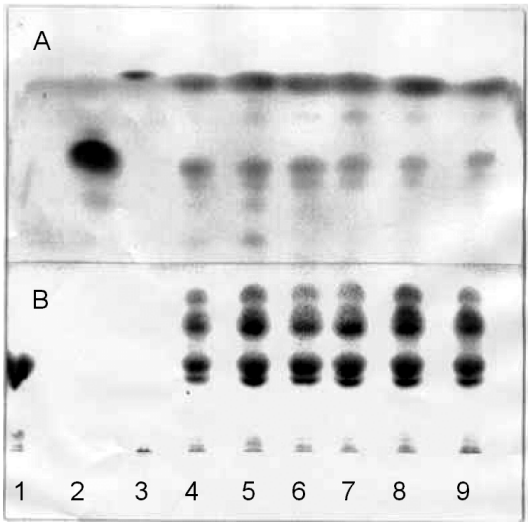

Fig. 3. TLC of unsaponifiable matter in sunflower oils with different processing conditions Plate: Silica gel 60 (0.25 mm "Merck"); solvent system – hexan-diethylether (65:35); reagent spray – α, α' dipyridil-ferrum (A); anisaldehyd (B); 1: cholersterol; 2: α-tocopherol; 3: β-carotene; 4: deodorized; 5: crude; 6: cold pressed in factory; 7: hot pressed in laboratory; 8: cold pressed in laboratory; 9: extracted in laboratory

Figure 3 shows that there are no greater differences in composition of unsaponifiable matter of oil samples. Tocopherols were detected in all refined and non-refined oils, but probably with different concentration. The quantity of tocopherols was not determined in these samples.

According to the results of JUNG and MIN (1990), tocopherols act as antioxidants or prooxidants depending on their concentration. The optimal concentrations of α-, γ-, and δ-tocopherols to increase stability of purified soybean oil were 100, 250 and 500 ppm, respectively. They had a prooxidant effect at higher concentrations above this. LAMPI and co-workers (1999) found that at lower levels (≤50 μg g^{-1}) α-tocopherol was a more effective antioxidant than γ-tocopherol, but at higher levels (>100 μg g^{-1}) γ-tocopherol was more effective. No prooxidative effect of either tocopherol was found at any addition level.

3. Conclusions

Refining process of sunflower oil had a great influence on oxidative changes, as well as on pigment and sterols content. In the course of refining, PV was decreased and conjugated products were increased, especially during bleaching process, which is evident from high absorbance values at 270 nm for BO and DO. The values of these

measurements can indicate addition of refined oil into non-refined oil. Between hot (LHPO) and cold (LCPO) pressed oil there are no major differences in oxidative degradation.

The major carotenoids in sunflower oil are xantophylls (predominantly dihydroxy carotenoids). During refining process they are almost totally removed (86% decrease).

The highest level of total sterols was present in industrial crude oil (CO), which was obtained by combined procedure of pressing and hexane extraction. After refining the losses of sterols amounted to 22%, most of which (19%) was caused by the effect of bleaching. Among individual sterols, the highest degradation occurred to β-sitosterol, which is the most represented sterol in sunflower oil.

Hot pressed oil (LHPO) had somewhat greater content of sterols than cold pressed (LCPO) and extracted (LEO) oils. Sterols are heat stable molecules and according to GROB and BRONZ (1994), the presence of degradation products is not the result of seed heating during oil manufacture.

Sunflower oil differs from most other oils in its high concentrations of Δ^7-sterols, in particular Δ^7-stigmasterol.

LEO had the longest induction periods with an average of 13.9 h under the preset Rancimat conditions, followed by 9.8 h for DO, and the shortest had CPO and LCPO with 7.5 h.

Refining of sunflower oil does not bring about a great reduction of tocopherols, moreover peroxides were removed, which resulted in higher oxidation stability of deodorized than crude oil.

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