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Relationships between quality of crude and refined edible oils based on quantitation of minor glyceridic compounds

M. V. Ruiz-Méndez, G. Márquez-Ruiz & M. C. Dobarganes*

Instituto de la Grasa (CSIC). Avda. Padre García Tejero, 4, 41012-Sevilla, Spain

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The relationships between crude and refined oils are examined by quantitation of minor glyceridic compounds, namely, oxidized triglyceride monomers, dimers and diglycerides, associated with oil quality. Particularly, two groups of compounds, i.e. oxidized triglyceride monomers and diglycerides, are of especial interest as they are indicative of oxidative and hydrolytic alterations, respectively. Olive, sunflower and soybean oils differing in initial quality, as evaluated by classical indices and levels of undesirable minor compounds, were subjected to physical and alkali refining in a laboratory system. In all assays, results indicated that amounts of oxidized triglyceride monomers and diglycerides in refined oils remained close to those found in the starting crude oils. Triglyceride dimers were the only group of compounds showing a significant increase, which was dependent on fatty acid composition and initial quality of crude oils. The main conclusion is that quantitation of minor glyceridic compounds in refined oils not only offers a new possibility for quality evalution but also allows the crude oils to be characterised by the presence of markers of oxidative and hydrolytic alterations. © 1997 Elsevier Science Ltd

INTRODUCTION

The aim of the refining process is to remove undesirable compounds in order to improve quality. Separation of phospholipids, free fatty acids, pigments and volatile compounds responsible for off-flavours are foreseen in the different steps of the process, although some unwanted non-volatile compounds might remain at the end of the process. The changes in minor compounds taking place during refining have been extensively studied (Mount, 1981; Sleeter, 1981; Kochhar, 1983; Jaward *et al.*, 1984; Jung *et al.*, 1989; Lanzón *et al.*, 1994; Schulte, 1994). Quality depends on the technology used as well as on the quality of the raw material (Helme, 1980; Naudet *et al.*, 1982; Bagge, 1992; Gupta, 1993; Lanzani *et al.*, 1993). Nevertheless, changes occurring during refining have not been translated into useful information about the starting quality of the crude oil.

In a previous short communication (Dobarganes *et al.*, 1990), we emphasized the importance of minor polar compounds, derived from glycerides, for quality evaluation of refined oils. Changes during the stages of the alkali refining process were evaluated, which mainly resulted in the formation of polymerization compounds during deodorization and the loss of free fatty acids during neutralization. Similar results were obtained on industrial refined oils (Hopia, 1993).

The objective of this paper is to contribute to a better knowledge of the relationships between crude and refined oils based on the amounts of oxidized triglycerides and diglycerides which remain after refining as markers of oxidative and hydrolytic alterations. With this objective, oils which differed in fatty acid composition and initial quality were subjected to both alkali and physical refining in order to combine the main variables that may influence the contents of minor glyceridic compounds in crude oils and/or their changes during refining.

MATERIALS AND METHODS

Six lots of crude olive (OO), sunflower (SFO) and soybean (SBO) oils were alkali- and physically-refined using a discontinuous laboratory system. Fatty acid composition of initial oils is shown in Table 1. The oils were processed by refining and then analysed.

*To whom correspondence should be addressed.

Alkali refining

Degumming

1 kg of crude oil was charged into a 2 litre, three-necked, round-bottomed stirred tank reactor, with an outlet in the lower part, fitted with a thermometer and a stirring shaft with a Teflon blade driven by a 170 rpm stirring motor. After the contents were purged with nitrogen, the stirring motor was started and the oil temperature was brought to 40°C. The degumming agent, phosphoric acid 50% w/w, was added at a concentration of 0.2% w/w. It was stirred for 20 min at 40°C. Gums were not separated.

Neutralization

The contents were heated to 60°C under a nitrogen blanket. The required amount of 18°Bé and 10% of excess lye was added. Then the contents were brought to 80°C and, after being stirred for 10 min at this temperature, the soap stock was separated from the refined oil by decantation and centrifugation. The oil was washed three times with water (20% w/w).

Bleaching

The oil was brought to 80°C under a nitrogen blanket and 0.5% w/w of bleaching earth (Superactivated Type C; Minas de Gado S.A., Almería, Spain) was added. Once this temperature was reached, the oil was held for 15 min more with magnetic stirring, cooled and filtered through paper.

Deodorization

Degummed, refined, bleached oils were deodorized in glass laboratory equipment. The deodorization was conducted under a vacuum of less than 3 Torr and the steam flow was 2 % h^{-1} in all the assays. The temperature was 260°C and initial heating time to reach the selected temperature was 20 min, approximately. After 3h at 260°C, the oil was allowed to cool and vacuum was released with nitrogen. Small intermediate samples were taken out after 1 and 2 h of deodorization.

Physical refining

The process consisted of the same stages described above except for the neutralization step, since free fatty acids were removed here in the last step by steam-distillation. After degumming, phospholipids were separated and oils were washed three times with 10 % water (w/w) at 60°C. For bleaching, 1.5% (w/w) of bleaching earth (Superactivated Type C; Minas de Gador S.A., Almería, Spain) was used. Finally, oils were deodorized under the conditions described above for alkali refining.

Table 1. Fatty acid composition (%) of crude oils

	OO 1	OO 2	SFO 1	SFO 2	SBO 1	SBO 2
C16:0	11.4	11.7	7.4	7.0	11.2	12.0
C16:1	1.1	1.3	—	—	—	—
C18:0	2.3	1.8	4.4	4.6	3.3	3.6
C18:1	72.6	75.6	32.2	30.4	27.5	22.6
C18:2	11.0	8.2	54.6	57.1	50.8	54.7
C18:3	0.7	0.6	—	—	6.6	6.5
Others	0.9	0.8	1.4	0.9	0.6	0.7

Abbreviations: OO, Olive Oil, SFO, Sunflower Oil, SBO, Soybean Oil.

Analytical determinations

Samples of crude and deodorized oils were analyzed by the following method: Total Polar Compounds (PC) were determined by means of silica column chromatography, following the standard method (IUPAC, 1987). The efficacy of the separation was checked by thin-layer chromatography to guarantee the absence of non- polar triglycerides in the polar fraction.

PC were separated by high performance size-exclusion chromatography (HPSEC) (Dobarganes *et. al.*, 1988). The samples were analyzed in a Konik 500 A chromatograph (Konik S.A., Barcelona, Spain) with a 10-μl sample loop. A Hewlett Packard 1037 A refractive index detector (Hewlett Packard, Pittsburgh, PA, USA) and two 100 and 500 Å PL-gel columns (0.77×30 cm) (Hewlett Packard, Pittsburgh, PA, U.S.A.) connected in series were operated at 35°C. Peaks areas were determined using a Hewlett Packard 3390 A integrator. HPLC-grade tetrahydrofuran served as the mobile phase with a flow of 1 ml min^{-1} and sample concentration was between 5 and 15 mg ml^{-1} in tetrahydrofuran. Under these conditions, resolved peaks of triglyceride dimers (TGD), oxidized triglyceride monomers (ox TGM), diglycerides (DG) and fatty acids (FA) were obtained.

Determinations of phosphorus, free fatty acids, colour, stability and unsaponifiable matter were carried out according to standard methods (AOCS, 1987).

RESULTS AND DISCUSSION

Table 2 shows changes in physical and chemical characteristics of the six oils after alkali-and physical-refining. Data for phosphorous, colour and free FA indicate a good efficiency of degumming and bleaching in both refining systems as well as an effective elimination of FA during neutralization and deodorization steps in alkali- and physical-refining, respectively. Results correspond to samples deodorized for 3 h at 260°C, although analyses of intermediate samples, obtained after heating during 1 and 2 hr demonstrated that oils OO 2, SFO 2, SBO 1 and SBO 2 were properly deodorized just after 1 h. In the cases of crude oils of very low quality, i.e. OO 1 and SFO 1, 2 h were necessary. Nevertheless, deodorization was carried out for 3 h in order to obtain comparative samples from alkali-and physical-refining, since decrease of free FA by distillation to acceptable levels (< 0.2%) required 3 h under the conditions applied.

The main differences between the two refining systems were found in colour and unsaponifiable fractions.

Table 2. Physical and chemical characteristics of crude and refined oils

		Phosphorus (ppm)	Acidity (%)	Colour*	Stability (h)	Unsaponifiable Matter (%)
OO 1	Crude	6.5	6.38	79/1.7	8.3	1.18
	Alkali-Refined	<2	0.05	10/0.5	9.7	0.77
	Physically-Refined	<2	0.04	35/1.2	8.4	0.83
OO 2	Crude	<2	1.17	70/3.0	29.4	1.45
	Alkali-Refined	<2	0.14	3/n.d.	13.6	1.16
	Physically-Refined	<2	0.05	10/0.4	13.4	1.31
SFO 1	Crude	52	1.58	35/3.5	9.5	1.17
	Alkali-Refined	<2	0.12	10/1.3	6.8	0.81
	Physically-Refined	<2	0.17	10/1.4	5.6	0.99
SFO 2	Crude	54	0.76	30/3.0	9.1	0.98
	Alkali-Refined	<2	0.05	10/0.7	7.4	0.72
	Physically-Refined	<2	0.06	10/0.4	7.3	0.79
SBO 1	Crude	86	1.30	70/9.2	14.4	0.88
	Alkali-Refined	<2	0.02	10/0.9	9.1	0.61
	Physically-Refined	<2	0.11	10/1.5	12.2	0.75
SBO 2	Crude	584	1.19	70/8.6	5.0	0.78
	Alkalin-Refined	<2	0.02	10/0.6	10.4	0.65
	Physically-Refined	<2	0.14	10/1.9	7.8	0.66

For abbreviations. see Table 1.
*Lovibond (5 1/4″) Yellow/Red.

Slightly darker oils were obtained in physical refining in spite of the higher content of bleaching earth used (1.5% vs. 0.5% w/w) indicating that a significant bleaching effect took place during neutralization (Strecker *et al.*, 1983; Hendrix, 1990). Similarly, higher amounts of unsaponifiable fractions remained after physical refining. As has been reported previously, this is probably due to the loss of sterols, hydrocarbons and alcoholic compounds during the treatment with alkali (Lanzón *et al.*, 1987, 1994; Serani & Piacenti, 1992).

However, results obtained for oxidative stability are dfficult to explain. On the one hand, removal of free FA would increase stability as they are oxidized more rapidly than those FA esterified in triglycerides (Miyashita & Tagaki, 1986; Mistry & Min, 1987). On the other hand, antioxidants are partially removed and this would contribute to decreasing stability (Jung *et al.*, 1989; Ludwicki *et al.*, 1986; Maza *et al.*, 1992; Yoon & Kim, 1994). In consequence, changes in susceptibility to oxidation would depend on changes in total pro-oxidants and anti-oxidants, whose levels are very variable in crude oils and difficult to evaluate.

In summary, results from Table 2 indicated that standard quality refined oils were obtained independently of the type of refining and of the crude oils but such analytical determinations did not establish any relationship between crude and refined oils.

Table 3 shows quantitation of total PC after separation by silica column and their distribution evaluated by HPSEC. An HPSEC representative chromatogram is presented in Fig. 1, where four main peaks eluting in inverse order of molecular weight are resolved: TGD, characteristic of thermal degradation; oxTGM, related to oxidative alteration; DG; and FA, these latter two mainly produced through hydrolytic reactions. The FA peak also includes a part of the polar unsaponifiable fraction and, in consequence, is of no practical interest from a quantitative point of view. Thus, the main groups of PC resolved are glyceridic compounds associated with the main alterations in fats and oils.

The first column of Table 3 shows the PC percentages for crude and refined oils. The amounts of PC were very different between the two samples of olive oil (OO 1 and OO 2) and sunflower oils (SFO 1 and SFO 2) while they were of the same order for SBO 1 and SBO 2. Considering that total PC are essentially alteration compounds, the higher the PC percentages, the lower the expected quality of the oils. Hence, OO 1 and SFO 1 would be the oils of lowest quality among the ones selected. As can be observed, after alkali- or physical-refining, changes in PC followed a different pattern depending on the oil. PC percentages decreased in olive oils — drastically in OO 1 and slightly in OO 2 — while they tended to increase in sunflower and soybean oils.

Only further quantitation of the main groups of minor glyceridic compounds could provide an explanation for the changes obtained in total PC. It was interesting to note that equal amounts of PC in crude OO 1 and SFO 1 corresponded to quite different distribution of compounds. DG and FA comprised almost 90% of crude OO 1, while the major compounds in SFO 1 were oxTGM. After refining, the removal of FA contributed to the drop of PC in OO 1, while oxTGM remained due to their lower volatility, mostly accounting for the high values of PC in refined SFO 1.

Table 3. Total Polar Compounds (wt% on oil) and Polar Compound Distribution (mg g^{-1} oil) in crude and refined oils

		Polar Compounds				
			Distribution			
Sample		Total	TGD	oxTGM	DG	*FA
OO 1	Crude	13.9	—	16.5	57.5	65.0
	Alkali-Refined	8.0	18.9	14.4	41.8	4.9
	Physically-Refined	8.6	14.1	10.0	53.6	8.3
OO 2	Crude	4.0	—	6.3	22.0	11.7
	Alkali-Refined	3.5	6.5	5.9	18.9	3.7
	Physically-Refined	3.7	5.4	5.2	20.9	5.5
SFO 1	Crude	13.9	1.6	107.1	12.5	17.8
	Alkali-Refined	14.5	43.7	86.3	11.2	4.1
	Physically-Refined	14.2	47.8	76.5	12.5	5.2
SFO 2	Crude	5.5	0.9	32.1	11.5	10.5
	Alkali-Refined	7.0	23.6	31.0	10.9	4.5
	Physically-Refined	6.4	20.0	27.3	11.5	5.1
SBO 1	Crude	7.1	1.5	37.0	15.5	17.0
	Alkali-Refined	8.5	28.2	36.1	15.0	5.7
	Physically-Refined	8.7	29.3	34.7	16.8	6.2
SBO 2	Crude	7.9	1.0	44.9	15.0	18.1
	Alkali-Refined	8.7	28.7	40.1	14.3	3.9
	Physically-Refined	8.6	23.2	39.5	16.9	6.4

*FA. Fatty acids and polar unsaponifiable matter.
For other abbreviations. Table 1 and Fig. 1.

In general, evaluation of minor glyceridic compounds in initial oils indicated that the predominant compounds were oxTGM in polyunsaturated oils, and DG plus FA in monosaturated oils, independently of the PC percentages. After refining, the loss of FA and formation of polymerization compounds clearly supported the changes observed in polar compound percentages, since the amounts of oxTGM and DG were similar to those present in starting crude oils, thus remaining as markers of oxidative and hydrolytic alterations, respectively, in crude oils.

With respect to the influence of the type of refining, the main differences were found in the content of DG, higher in physical-refining. In the case of refined soybean oils, the amounts of DG were even slightly higher than those found in the crude oils. These results suggest that a small loss of DG took place during neutralization apart from the occurrence of thermolytic and hydrolytic reactions, as previously reported at this temperature and under high vacuum (Szabo Sarkadi, 1959; Nawar, 1985). Higher values were also obtained for the peak including FA and polar unsaponifiable fractions after physical refining, which is consistent with the data included in Table 2 for unsaponifiable matter.

Influence of fatty acid composition and initial quality on the changes of minor glyceridic compounds during refining was specifically noted in the formation of polymerization compounds. Crude oils presented very low contents of TGD, which were not even detectable in olive oils. As is known, polymerization takes place at high temperatures and depends on the unsaturation degree of oils (Eder, 1982; Dobarganes & Pérez-Camino, 1987), which explains why lower levels were found in olive oils as compared to sunflower and soybean oils. Nevertheless, in spite of the similar fatty acid

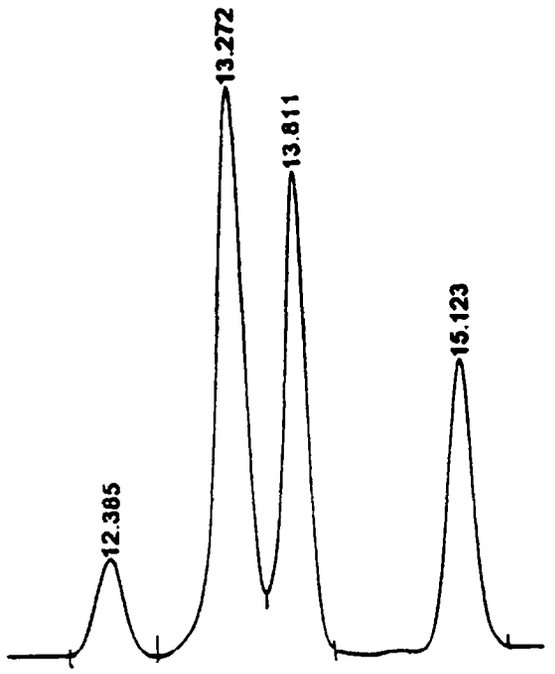

Fig. 1. Efficacy of HPSEC separation of Polar Compounds in a refined oil. Retention time (min): 12.4, TGD (triglyceride dimers); 13.3, oxTGM (oxidized triglyceride monomers); 13.8, DG (diglycerides) and 15.1, FA (fatty acids) and unsaponifiable fraction.

Table 4. Total Polar Compounds (wt% on oil) and Polar Compound Distribution (mg g^{-1} oil) during deodorization of sunflower oils

			Polar compounds				
				Distribution			
		Time (h)	Total	TGD	oxTGM	DG	*FA
SFO 1	Crude		13.9	1.6	107.1	12.5	17.8
	Alkali-Refined	1	13.9	26.7	93.7	11.9	6.7
		2	14.0	34.3	88.4	11.2	6.1
		3	14.6	43.7	86.3	11.2	4.8
	Pysically-Refined	1	13.9	27.1	88.0	13.2	10.7
		2	14.2	38.5	82.0	13.3	8.2
		3	14.2	47.8	76.5	12.5	5.2
SFO 2	Crude		5.5	0.9	32.1	11.5	10.5
	Alkali-Refined	1	6.2	14.7	31.6	10.2	5.5
		2	6.6	19.9	30.8	10.4	4.9
		3	7.0	23.6	31.0	10.9	4.5
	Physically-Refined	1	6.3	13.8	30.1	11.7	7.4
		2	6.4	17.6	29.0	11.6	5.8
		3	6.4	20.0	27.3	11.6	5.1

*FA. Fatty acids and polar unsaponifiable matter.
For other abbreviations. see Table 1 and Fig. 1.

composition, the amount of TGD after refining in OO 1 was three- fold higher than in OO 2. In the case of SFO 1, formation of dimers was also much more relevant than in SFO 2 and soybean oils. Apparently, the formation of TGD in the oils with initial low quality, i.e. OO 1 and SFO 1, was parallel to a decrease in the amounts of oxTGM.

To clarify this point, intermediate samples taken out after 1 and 2 h of deodorization were analyzed. Table 4 lists the evolution of PC and distribution of minor glyceridic compounds in sunflower oils. As expected, the longer the heating time, the higher the amount of TGD formed. However, the main increase was obtained after 1 h at 260°C, probably due to both the 20 min initial heating period to reach the selected temperature and the availability of higher levels of oxygen during the initial heating period. It is interesting to observe the continuous decrease of oxTGM in SFO 1, which would indicate their participation in polymerization reactions.

oxTGM is a complex group of monomeric triglycerides containing, at least, one oxygenated function, i.e. hydroperoxides, epoxides, ketones, etc. (Frankel, 1985). The results obtained would indicate that some of these compounds could be more susceptible to undergo polymerization at high temperatures through oxygenated linkages than are the non-polar fatty acids through C-C linkages. Thus, the higher amounts of TGD in SFO 1, as compared to SFO 2, seemed to result from the decrease of oxTGM, although, as calculated from the initial and final amounts, 19.4 and 28.6 were the maximum percentages lost in chemical- and physical-refining, respectively, while the major part of the high amounts present initially remained in the refined oils.

In summary, the results obtained in this study indicated that, independently of the refining system, fatty acid composition and initial quality of the oils, the amounts of oxTGM and DG remained close to the levels found in crude oils. Thus, oxidation and hydrolysis in oils subjected to refining can be deduced from the analysis of the refined oils.

More specifically, high levels of DG in refined oils would indicate higher percentages of total PC in crude oils, due to the initial presence of significant amounts of free FA eliminated during refining, while high levels of oxTGM in refined oils would suggest their participation in the formation of polymerization compounds.

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