Oxidation of Sunflower Oil During Storage

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ABSTRACT: Effects of temperature and oxygen concentration on oxidative deterioration during storage of crude sunflower oils, obtained by pressing and solvent extraction, were studied. Oxidation was monitored through several analytical and chromatographic methods that determine chemical and physical changes or analyze specific oxidation compounds at different stages of the process: peroxide value, *p*-anisidine value, free fatty acids, weight gain, total content and distribution of polar compounds, and composition of fatty acids. Extracted oil showed a higher oxidative stability than pressed oil. Oxidative deterioration was strongly dependent on temperature, oxygen availability, and the ratio of exposed surface to sample volume. A kinetic model of two series reactions was developed to represent oxidation rate in terms of peroxide value, the reaction rate constants and their temperature dependence being evaluated by nonlinear regression. Finally, good correlations between the percentage of polar compounds or oxidized triglyceride monomers and the peroxide value were found.

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KEY WORDS: Autoxidation, HPSEC chromatography, oxidation rate, oxygen availability, peroxide value, polar compounds, temperature effect, sunflower oil.

Crude sunflower oil is produced at the crushing plants by mechanical pressing and hexane extraction, followed by water degumming. Most crude oils are exposed to changing temperatures during the relatively long times before refining, in storage tanks, and/or in ships' holds during transportation. Autoxidation or oxidative rancidity is the major cause of quality losses in crude and refined oils during storage. Oxidative stability and deterioration of oils depend on initial composition, concentration of minor compounds with antioxidant or prooxidant characteristics, degree of processing, and storage conditions. The consequence of oxidation is the development of unpleasant tastes and odors, characteristic of rancid fats and oils, as well as degradation of functional and nutritional properties.

Autoxidation of unsaturated lipids is a catalytic process involving a free-radical chain reaction mechanism, with formation of hydroperoxides, and further reactions of oxidation, breakdown, and polymerization. These reactions originate a complex mixture of intermediate and final products (1–4). The mechanism of lipid oxidation changes significantly at elevated temperatures and depends strongly on oxygen availability. Therefore, marked differences in oxidative stability and deterioration rates can be obtained depending on analysis conditions. Various methods are currently used to evaluate the oxidation of lipids, which can be assessed by monitoring organoleptic properties or different chemical and physical changes (2–6). Most available methods can be classified as those that measure either primary or secondary changes. The primary oxidative products can be monitored through peroxide value (PV), weight gain, loss of unsaturated fatty acids, conjugated diene value, and others. Secondary changes are generally measured by *p*-anisidine value (AV), thiobarbituric acid test, and chromatographic techniques that analyze specific oxidation compounds. However, there is no standard method to detect oxidative changes during the entire process, and a combination of different analytical techniques is usually required (2–4). Some of these methods have been used to evaluate stability and oxidation of refined sunflower oils (7–11), but little is known on the behavior of crude sunflower oil.

During the last years, a methodology based on a combination of adsorption and size exclusion chromatography has been applied to study alteration of used frying oils, quality of refined oils, and oxidation compounds in fats and fatty foods (12–17). This methodology provides better knowledge of the thermoxidative alteration of lipids, enabling the concomitant evaluation of initial and decomposition compounds through quantitative determination of oxidized triglyceride monomers and triglyceride dimers. The method has been used successfully to evaluate changes in refined sunflower oils during autoxidation (14), processing or refining (15), conventional and microwave heating (17), and frying (13). In contrast, applications to analyze alterations during extraction and storage of crude oils are scarce.

The main objective of this work was to study the oxidative deterioration during storage of crude sunflower oils, obtained by pressing and solvent extraction, by using different methods and analyzing the influence of composition, temperature, and oxygen concentration.

EXPERIMENTAL PROCEDURES

Performance of storage experiences. Industrial samples of crude sunflower oil obtained by pressing (P) and hexane extraction (E), which had been water degummed, were used. Oil samples were kept in 100-mL caramel-colored glass bottles of 4 cm i.d., the oil surface area exposed to the atmosphere being approximately 12.5 cm^2, and heated at different temperatures in

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standard laboratory ovens. Storage experiences were carried out at 30, 47, and 67°C, using open flasks (o) and capped flasks (c) with different amounts of oil or under nitrogen atmosphere. The oil weights used in capped flasks (22.5, 45, and 90 g of oil) give air/oil volumetric ratios of 3.10, 1.06, and 0.03, respectively. Samples were withdrawn periodically from the oven and were stored at 5°C under nitrogen atmosphere for further analysis.

Standard AOCS (5) and IUPAC (6) official methods were used to determine acidity or free fatty acids (FFA) (IUPAC 2.201), PV (AOCS Cd 8-53), AV (AOCS Cd 18-90), and total phosphorus content (AOCS Ca 12-55). The oxidative stability index, represented as induction time in hours, was measured with a Metrohm 679 Rancimat (Metrohm, Herisau, Switzerland), at 98°C and 20 L/h airflow. In addition, an analytical MettlerPC180 balance (Mettler-Toledo International, Inc., Zürich, Switzerland) with precision of ±0.001 mg was used for gravimetric monitoring of oxidation.

Gas chromatographic analysis of fatty acid esters. Fatty acid composition was determined by gas chromatography of the methyl esters according to IUPAC 2.301-2.302 methods (6), using a Varian 3700 equipment (Varian Associates Inc., Palo Alto, CA) with flame-ionization detector and a tubular column 10% GP-DEGS-PS (L = 2 m, i.d. = 0.32 cm).

Tocopherol content . Tocopherol was measured by high-performance liquid chromatography (HPLC) using AOCS Ce 8-89 method (5). A Varian Vista 5500 HPLC system with fluorescence detector and a LiChrosorb Si-60 (250 × 4 mm, 5 µm particle size) column (Merck, Darmstadt, Germany) were used.

Determination of polar compounds. The polar fraction was isolated by means of column chromatography and determined gravimetrically according to IUPAC 2.501 standard method (6). The efficiency of column separations was confirmed by thin-layer chromatography (TLC) for the absence of nonpolar triglycerides in the polar fraction. The nonpolar fraction was further analyzed by gas chromatography to determine its fatty acid composition.

Polar compound distribution. The altered compounds that constitute the polar fraction were separated into polymers and dimers of triglycerides, oxidized triglycerides, diglycerides, and free fatty acids by high-performance size-exclusion chromatography (HPSEC) according to the Dobarganes *et al.* method (12). A Waters 600E chromatograph (Waters Associates, Milford, MA), a Varian series RI-3 refractive index detector, one 100- and one 500-Å Ultrastyragel columns (Waters Associates) connected in series were used. The columns were 25 × 0.77 cm i.d., packed with a porous, highly cross-linked styrenedivinylbenzene copolymer (<10 µm). HPLC-grade tetrahydrofuran served as the mobile phase with a flow of 1 mL/min.

RESULTS AND DISCUSSION

The initial characteristics of different water-degummed, nonrefined sunflower oils used in this study are shown in Table 1. This information allows us to analyze the influence of oil composition and the presence of minor components on the oxidative process.

Effect of type of storage conditions on evolution of PV and AV in sunflower oils is shown in Figures 1 to 3, respectively. As expected, peroxide formation increased notably with temperature (Fig. 1), oxygen availability (Fig. 2), and amount of oil or air to oil ratio (Fig. 3). Oil heated at 30°C showed relatively low oxidative deterioration. No significant oxidation, as measured by PV and AV, was observed in samples stored under nitrogen atmosphere or with low oxygen concentration (90 g of oil in capped flasks). PV increased progressively during storage in all samples except those stored at 67°C which presented a maximum in PV and thereafter decreased as the decomposition reactions became prevailing (Fig. 1). Hydroperoxides are the primary products formed during oxidation, but they are labile intermediate compounds that decompose into several secondary oxidation products. Thus, even though PV is a common indicator of lipid oxidation, its use is limited to the earlier stages of oxidation (2–4). AV, an indicator of the aldehyde content (principally as 2-alkenals and 2,4-dienals), remained practically constant at the earlier stages of oxidation, but then increased sharply following the decomposition of peroxides (Figs. 1–3). Apparently, the maximum value reached in PV tends to decrease with the temperature of oxidation, suggesting that the activation energy for the decomposition reaction is higher than that for the production of hydroperoxides.

Topallar *et al.* (11) observed that autoxidation of refined sun-

TABLE 1
General Characteristics of Sunflower Oils

	Pressed		Extracted
Analytical determination	Sample 1	Sample 2	Sample 3
Free fatty acids (% oleic acid)	0.67	0.90	1.07
Peroxide value (meq/kg)	2.45	3.92	3.36
p-Anisidine value	0.96	1.27	1.91
Oxidative stability (h at 98°C)	13.7	12.8	14.7
Polar compounds (wt%)	4.20	4.80	5.69
Fatty acid composition (%)			
$C_{16:0}$	6.26	6.53	7.61
$C_{18:0}$	3.21	3.88	2.79
$C_{18:1}$	22.77	21.19	18.60
$C_{18:2}$	67.86	68.39	70.99
Tocopherol content (mg/kg)	α: 723; β: 41	α: 701; β: 38	α: 703; β: 33
Total phosphorus (mg/kg)	52	42	67

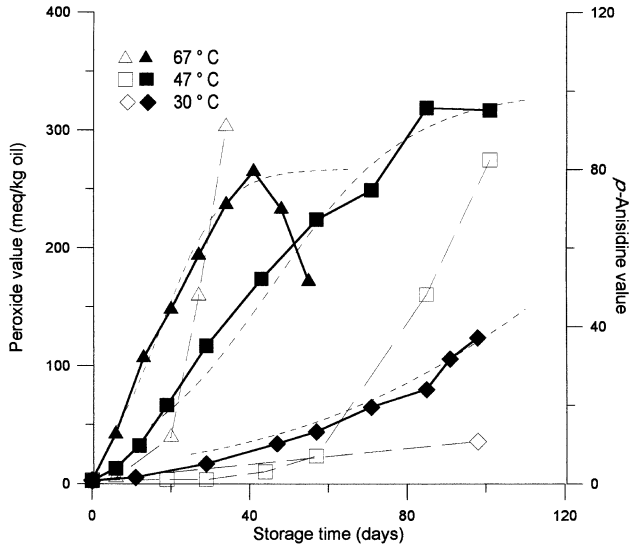


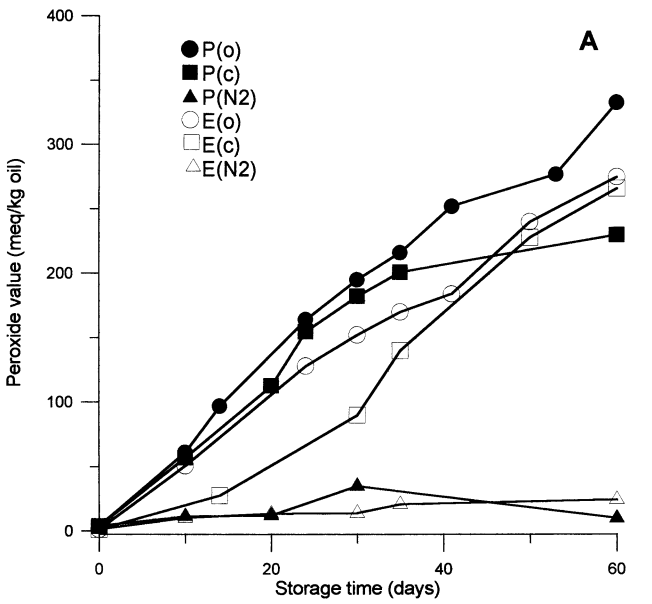
FIG. 1. Changes in peroxide value, experimental (—) and predicted by Equation 1 (----), and *p*-anisidine value (– –) during storage of pressed sunflower oil (sample 1) at different temperatures.

flower oil, kept in fully open containers and exposed to atmospheric conditions, depends on the concentration of hydroperoxides and follows first-order kinetics in terms of PV after the initial period. In our case, this simple model can be applied only at the lower temperature (30°C), resulting in $k_{PV} = 0.027\ d^{-1}$, a value significantly lower than those reported for refined oils (11). Discription of the kinetics must include peroxide decomposition reactions at higher temperatures.

Several sequential oxidation reactions fall into the category of series or consecutive reactions (18). The results of this study are better represented by a kinetic model composed of a first-order autocatalytic reaction and a second-order decomposition reaction, the temperature dependence of the reaction rate constants (k_1 and k_2) being expressed by an Arrhenius-type equation, as follows:

$$\frac{d\mathrm{PV}}{dt} = k_1\mathrm{PV} - k_2\mathrm{PV}^2;\ \ k_i = k_{oi}\exp(-\Delta E_i / RT) \qquad [1]$$

In these equations, k_{oi} and ΔE_i represent the frequency factor, and activation energy for the reaction rate constant k_i (i = 1,2), respectively; R the gas constant, and T the absolute temperature. Experimental data for sample 1 (Fig. 1) were correlated to the above expression using a quasi-Newton nonlinear regression technique to evaluate model parameters, resulting in $k_{o1} = 1.04 \times 10^5\ d^{-1}$, $\Delta E_1 = 38.35$ kJ/mol K, $k_{o2} = 0.139 \times 10^5\ (meq/kg\ d)^{-1}$, $\Delta E_2 = 48.47$ kJ/mol K. As shown in Figure 1, a reasonably good correlation between Equation 1 and experimental data was obtained for the three temperatures studied. The model applies from the critical PV at which this parameter starts to increase exponentially, which was found to be 18.8 meq/kg, up to the maximum PV. According to the model, PV reaches a steady-state value which is a function only of the rate constants. Predicted values are 414, 334, and 267 at 30, 47, and 67°C, respectively. The type of experimental behavior observed at 67°C,



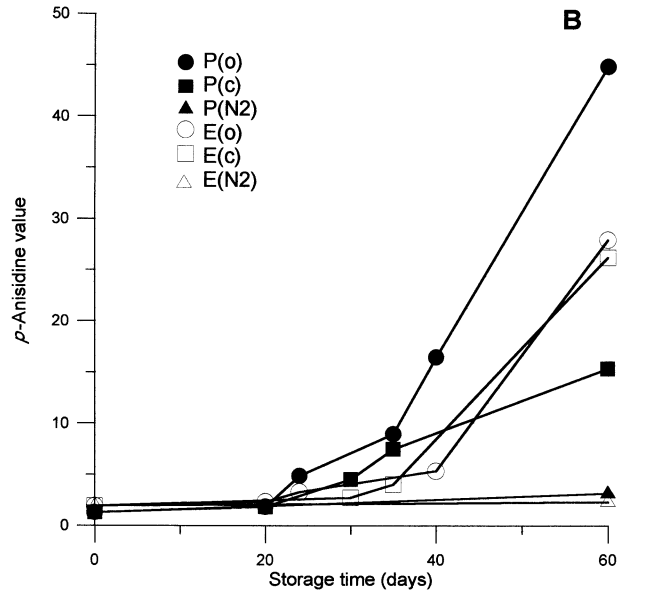


FIG. 2. Peroxide values (A) and *p*-anisidine values (B) of pressed and extracted sunflower oils stored at 47°C. Abbreviations: P = pressed oil, E = extracted oil, o = open flask, c = capped flask, N_2 = capped flask under nitrogen atmosphere.

with a maximum in the concentration of the intermediate species, is characteristic of series reactions with a continuous decay in the concentration of the reactive product (18). Applied to our case, it suggested that mass transfer (i.e., diffusion of unsaturated fatty acids and oxygen) may limit the oxidation rate at higher alterations.

When oxygen supply is practically unlimited, as in open flasks or with high air-to-oil ratios, oxidation rate depends on the relation between oil surface area exposed to air and sample volume. In fact, autoxidation was significantly higher for a capped flask with 22.5 g of oil than for an open flask with 45 g of oil at the same temperature (47°C). This can be explained in

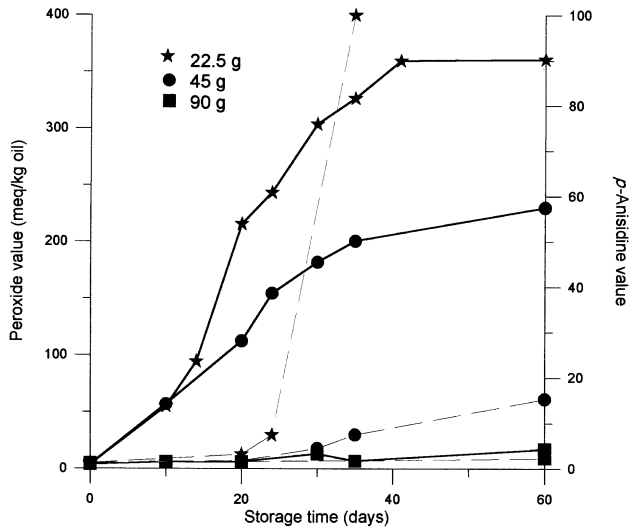


FIG. 3. Peroxide values (—) and *p*-anisidine values (– – –) of pressed sunflower oil stored at 47°C in capped flasks containing different amounts of oil.

terms of dissolution and diffusion of oxygen and dilution of oxidation compounds in the oil bulk.

Figure 2 shows that extracted oil had a lower oxidation than pressed oils under the same storage conditions. By comparison of samples 2 and 3 (Table 1), one can see that extracted oil also has the most advanced initial deterioration and a higher oxidative stability than pressed oil. Both oils have equivalent amounts of unsaturated fatty acids and the same concentration of tocopherols (natural antioxidants of vegetable oils), but extracted oil has a higher phosphorus content, which is related to the phospholipid content. Therefore, differences in oxidative stability could be attributed to the concentration of phospholipids, which have antioxidant synergistic activity and metal-scavenging capacity (19).

In most cases, FFA remained close to constant during storage, indicating absence of hydrolytic alteration (Tables 2 and 3). Only when deterioration was very high, i.e., at higher temperatures (67°C) or higher air-to-oil ratios (22.5 g of oil in capped flasks), was a clear increase in the acid value observed.

Figure 4 shows that the sample weight decreased slowly during the initial stages, and then increased continuously with

TABLE 2
Effect of Storage Temperature on Free Fatty Acid (FFA) Content (% oleic acid)

Storage at 30°C		Storage at 47°C		Storage at 67°C	
Days	FFA (%)	Days	FFA (%)	Days	FFA (%)
0	0.67	0	0.67	0	0.67
11	0.56	6	0.71	6	0.64
29	0.64	12	0.71	13	0.67
43	0.66	19	0.70	20	0.67
57	0.66	44	0.69	27	0.77
70	0.66	57	0.72	34	1.08
84	0.67	71	0.73	41	1.61
91	0.65	85	0.83	47	2.41
98	0.68	101	0.97	54	3.95

TABLE 3
Changes in Free Fatty Acids (% oleic acid) in Sunflower Oils Stored at 47°C

Time	Pressed oil				Extracted oil	
(d)	o[a]–45[b]	c[a]–22.5[b]	c[a]–45[b]	c[a]–90[b]	o[a]–45[a]	c[a]–45[b]
0	0.90	0.90	0.90	0.90	1.12	1.12
30	—	1.00	—	—	—	—
35	—	—	0.95	—	—	1.24
41	0.90	1.30	1.10	0.98	1.22	1.28
60	1.00	2.28	0.99	1.12	1.13	1.17

[a]Open (o) or capped (c) flasks.
[b]22.5, 45, or 90 g of oil in flasks.

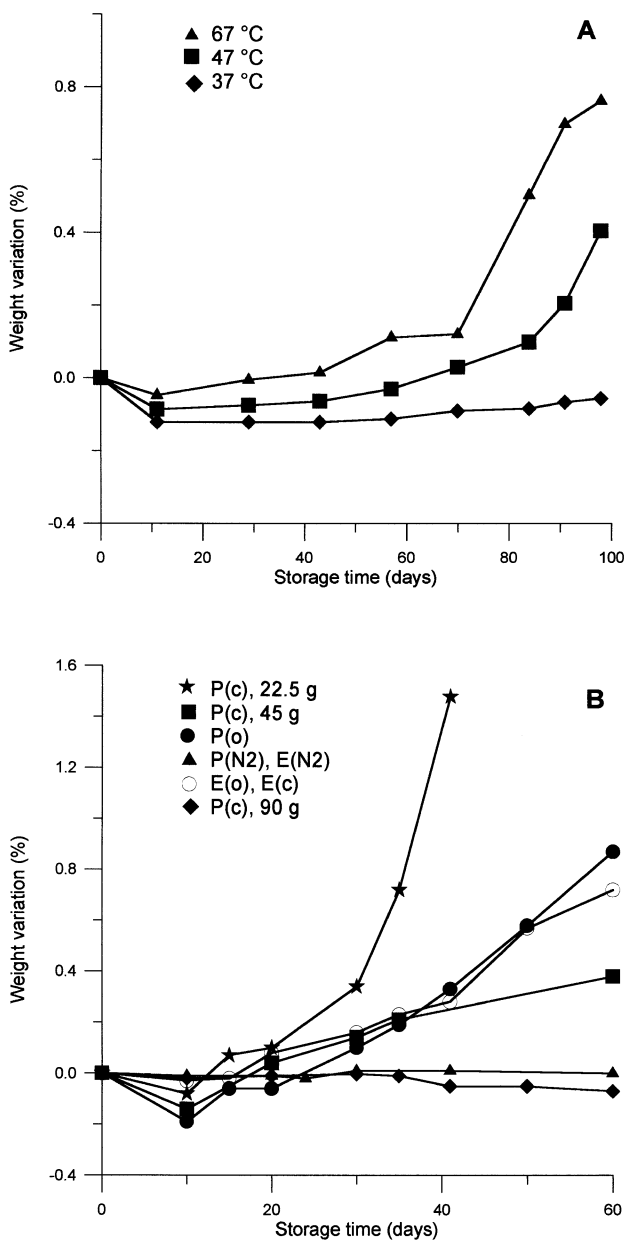


FIG. 4. Weight variation of sunflower oils stored at different conditions. Effect of temperature (A), oxygen availability and amount of oil (B). For abbreviations see Figure 2.

TABLE 4
Evaluation of Deterioration in Sunflower Oils During Storage[a]

Temperature (°C)	Time (d)	Test	PV (meq/kg)	AV	PC (%)	Polar compound distribution (%) TGP	TGD	OTG	DG	FFA
Sample 1—pressed oil										
	0		2.4	0.96	4.2	ND	ND	47.5	32.1	20.4
30	98	Open	125	1.28	10.8	ND	2.3	81.3	9.8	6.6
	98	N_2	4.4	1.04	8.1	ND	ND	39.6	35.9	24.5
47	19	Open	66.6	1.07	7.1	ND	1.5	74.5	13.2	10.8
	44	Open	174	3.09	13.5	ND	3.8	83.0	7.5	5.7
	101	Open	317	82.5	36.5	6.8	19.2	68.0	3.7	2.3
	101	N_2	14.5	6.20	14.2	ND	1.5	72.7	14.7	11.1
67	13	Open	107	3.31	9.2	ND	8.9	70.9	13.0	7.2
	27	Open	194	47.9	21.2	2.2	17.0	71.6	6.6	2.6
	41	Open	265	130	48.1	19.4	26.7	49.3	3.3	1.3
	54	Open	171	—	62.5	34.8	24.1	37.6	2.6	0.9
	54	N_2	5.40	3.57	11.9	ND	3.1	27.9	50.3	18.6
Sample 2—Pressed oil										
	0		3.92	1.27	4.8	ND	ND	66.2	17.1	16.7
47	24	Open	164	4.86	14.4	ND	10.1	78.9	5.7	5.3
	24	Capped	155	3.15	13.4	ND	5.0	83.7	6.3	5.0
	35	Open	216	8.96	18.6	ND	8.9	80.4	5.7	5.0
	35	capped	201	7.50	17.4	ND	8.0	81.0	6.3	4.7
Sample 3—Extracted oil										
	0		3.36	1.91	5.7	ND	ND	57.5	21.3	21.2
47	24	Open	128	3.28	12.0	ND	13.1	70.8	8.4	7.7
	30	Capped	90.0	2.75	11.2	ND	2.8	77.3	10.7	9.2
	50	Open	240	16.2	23.6	ND	13.6	76.2	5.7	4.5
	50	Capped	228	14.7	22.0	ND	10.1	80.1	5.1	3.9

[a]Abbreviations: PV = peroxide value, AV = anisidine value, PC = total polar compounds, TGP = triglyceride polymers, TGD = triglyceride dimers, OTG = oxidized triglyceride monomers, DG = diglycerides, FFA = free fatty acids, ND = not detected.

the oxidative process. The initial decrease of weight may be attributed to partial evaporation of humidity and other volatile compounds. As the oxidation proceeds, oxygen is incorporated into unsaturated fatty acids and more hydroperoxides are formed. There are also dimerization and polymerization reactions and oxygen uptake is faster, producing a weight gain. Weight remained practically constant in oil samples that experienced little or no oxidation.

Determination of the polar fraction constituted by oxidized triglyceride monomers (OTG), dimers of triglycerides (TGD) and polymers of triglycerides (TGP), diglycerides (DG), and FFA showed a progressive increase with time, temperature, and oxygen availability, following the same tendency found in other parameters (Table 4). The origin of deterioration can be evaluated from polar compound distribution. The OTG content is an indicator of oxidative alteration; the content of DG and FFA is related to hydrolytic alteration, and polymeric compounds (TGP and TGD) are useful to assess thermal alteration. Quantitation of oxidized triglyceride monomers and dimers is reported as a good measurement for early and advanced stages of oxidation since it provides information on the oxidation extent by evaluating concomitantly primary and secondary oxidation products (16). Initial contents of total polar compounds indicated a difference in the quality of the oils. Sample 1 had a slightly better quality than sample 2 while extracted oil (sample 3) had a higher oxidative and hydrolytic deterioration, which was also detected by PV, AV, and acidity analysis. As expected, no polymeric material (TGD and TGP) was detected in crude sunflower oils.

Data on the distribution of polar compounds showed that both oxidative and thermal degradation took place during storage, the former being the more important. A continuous increase in the level of OTG and TGD was observed in all samples and at all temperatures. Higher oligomeric compounds were detected at 67°C and in samples with high deterioration, demonstrating that some polymerization also occurs during autoxidation at relatively low temperatures (12,14,16). In samples stored at 30°C or under a nitrogen atmosphere, the TGD content was very low, which indicates that the oxidation process occurred in the early stages, as suggested by AV data. On the other hand, DG and FFA contents remained practically constant or changed slightly in most cases, showing little hydrolytic alteration during storage and confirming the findings for the AV. There were no significant differences in the DG and FFA of the open and capped flasks, but oils stored under nitrogen atmosphere showed some hydrolytic alteration at all temperatures.

Correlations between different determinations were analyzed. Polar compounds, especially OTG, increased closely parallel to PV during the first stages of oxidation and below the maximal PV. The following correlations of percentage of polar compounds (%PC) and percentage of oxidized triglyceride monomers (%OTG) with PV were found for this range (Fig. 5)

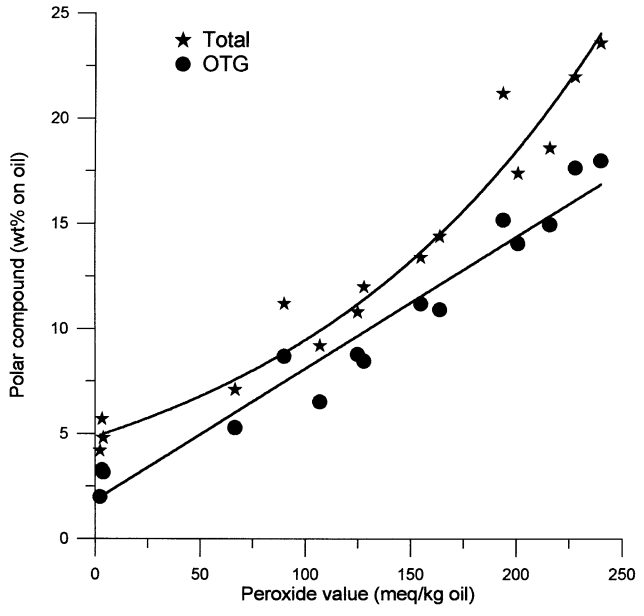


FIG. 5. Correlation between the percentage of total polar compounds or oxidized triglyceride (OTG) monomers and the peroxide value.

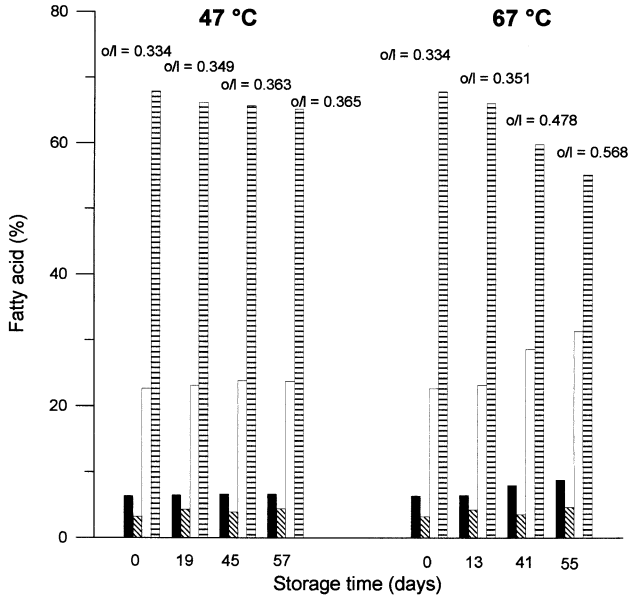


FIG. 6. Changes in fatty acid composition of pressed oil (sample 1) at 47 and 67°C. Solid box, palmitic acid; diagonally lined box, stearic acid; open box, oleic acid; horizontally lined box, linoleic acid. o/l = ratio between oleic acid and linoleic acid contents.

$$\%PC = 4.87 \exp[0.00665\ PV] \quad (r^2 = 0.963) \qquad [2]$$

$$\%OTG = 0.0627\ PV + 1.841 \quad (r^2 = 0.953) \qquad [3]$$

Note that the correlation between %OTG and PV is linear because both determinations measure primary oxidation products. On the other hand, %PC measures all products of thermoxidative deterioration and increased more steeply than PV.

Changes in fatty acid composition of the nonpolar fraction during storage can be observed in Figure 6. As alteration advanced, there was a continuous decrease of unsaturated fatty acids, particularly linoleic acid, being more pronounced at the highest temperature. It resulted in an increase in the oleic acid to linoleic acid ratio (o/l), indicating a preferential use of linoleic acid (18:2) in oxidation reactions. The relative rate of autoxidation of fatty acids increases with the polyunsaturate level, being approximately 100:1 and 1200:1 at 20°C for oleic/stearic acids and linoleic/stearic acids, respectively (20). A similar behavior was observed for pressed and extracted oils stored at 47°C in open and capped flasks. After 35 d of storage the o/l ratio increased from 0.31 to 0.34 in pressed oil, and from 0.26 to 0.31 in extracted oil.

In conclusion, the results showed the influence of storage temperature, oxygen availability, and oil composition on crude sunflower oil oxidation. Extracted oil has a higher oxidative stability during storage than pressed oil. Rate of oxidation is strongly dependent on oxygen concentration and temperature. Relatively low or no oxidation occurs at low temperatures, with limited oxygen availability, or under nitrogen atmosphere. A kinetic model for autoxidation of crude sunflower oil in terms of PV should consider both propagation and decomposition reactions. Alteration is affected by the ratio of surface area to volume of sample, indicating that the oxidative process may be limited by mass transfer phenomena as diffusion and dilution of reactants and products. Since no simple parameter provides enough information for a correct assessment of oxidation, it is necessary either to perform several analyses or to determine the composition of polar compounds in order to evaluate different stages of oxidation. In this study, good correlations between percentage of polar compounds or percentage of OTG and PV were found for the early stages of oxidation.

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