Comparison of the Frying Stability of Regular and High-Oleic Acid Sunflower Oils

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ABSTRACT: The frying stability of a regular sunflower oil (RSFO) was compared with that of a high-oleic acid sunflower oil (HOSFO). The rate of FFA formation was greater for HOSFO than RSFO during 72 h of frying. The content of tocopherols was much higher in RSFO and their degradation was markedly slower than that observed for HOSFO. The formation of total polar compounds, however, was similar for both oils despite the dramatic differences in FA composition. This study further confirms the limitations in predicting frying stability based solely on the FA composition and is consistent with earlier studies conducted in our laboratory.

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KEY WORDS: Frying stability, high oleic, regular, sunflower oil, tocopherols, total polars.

Recent studies conducted in our laboratory showed the limitations in predicting frying stability of vegetable oils based solely on FA composition (1,2). Minor components, particularly tocopherols, appear to have an important effect. Dobarganes and co-workers (3) compared three modified sunflower oils with olive oil. Two of the modified sunflower oils had higher total unsaturated FA and linoleic acid levels than olive oil. However, no significant differences were found between these oils with respect to the levels of total polar compounds (TPC) formed after heating at frying temperatures for 5 to 10 h. A third modified sunflower oil with levels of linoleic acid similar to olive oil had significantly lower TPC after 5 h of heating. These findings further suggested that the FA composition and degree of unsaturation are not sole predictors of the thermal stability of an oil. The authors indicated that such differences in stability might be due to differences in the FA distribution in the TG or in unsaponifiables such as hydrocarbons, higher alcohols, fat-soluble vitamins, and phytosterols (4). Przybylski and Zambiazi (5) confirmed that the content of FA only partially explained the storage stability of vegetables oils; the remainder of the variability was attributed to such minor components as tocopherols, sterols, and pigments. The present study compared the frying stability of a regular sunflower oil (RSFO) with that of a high-oleic acid sunflower oil (HOSFO).

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MATERIALS AND METHODS

Frying procedure and oil sampling. RSFO and HOSFO, both of which were refined by commercial processors and contained only MAG citrate as the added preservative, were studied. Each oil (2 L) was heated at 175 ± 2°C for 12 h/d for a total of 6 d in 2-L capacity domestic deep fryers (two SEB® brands; Selongey Cedex, Dijon, France). Fresh oils were placed in 30 mL glass vials, flushed with nitrogen, and stored at −20°C until analyzed. In addition, two 30-mL samples of each oil were taken at predetermined intervals throughout frying and stored in an identical manner. Each day, after 12 h of frying, the fryers were shut off and left to sit overnight. To accelerate the deterioration process, French fries were fried for 6 min each morning and evening. Russet-type potatoes were peeled and sliced into French fries using a Starfrit® potato chipper. A 1:6 ratio of food to oil was used based on that recommended by Morton and Chidley (6) and used by other researchers (7–9).

PV. PV were determined in duplicate by iodometric titration following AOCS Official Method Cd 8-53 (10).

FA analysis. FA were methylated prior to analysis by GC based on the AOCS Official Method Ce 1-62 (11). The conditions used were similar to those described previously by Normand *et al*. (1).

FFA. FFA were measured in duplicate as percentage of oleic acid by using the Veri-Fry® Pro-FFA-75 quick test method (Test Kit Technologies, Metuchen, NJ). A high coefficient of correlation (r^2 = 0.94) was reported previously between this method and the AOCS Method Ca 5a-40 (12).

Total polar compounds (TPC). TPC content was determined using Sep-Pak® Vac 6cc (1 g) cartridges (Waters Chromatography Division, Millipore Corporation, Milford, MA) to separate the polar from the nonpolar compounds. The procedure was carried as described by Petukhov (13), based on the method of Sebedio *et al*. (14). The percentage of TPC in the oil was determined by subtracting the weight of the nonpolar fraction from the initial weight of the oil, dividing this number by the initial weight of the oil, and multiplying by 100 based on the AOAC Method 982.27 (15).

Size exclusion chromatography. The composition of polar components formed during frying was analyzed using high-performance size exclusion chromatography (HPSEC). The polar fraction recovered from gravimetric assessment of this group of components was transferred from methanol into THF solution for HPSEC (16).

Separation was performed on a Shimadzu high-performance liquid chromatograph (model LC-10AD) with an ELSD. Components were separated on two size exclusion columns in series (Phenogel 5 100A and 500A; 300 × 4.6 mm; Phenomenex, Torrance, CA). The mobile phase was THF at a flow rate of 0.3 mL/min, and a 30 μL sample was injected. The ELSD was operated at 50°C with a nitrogen flow of 1 L/min.

Tocopherols. Tocopherols were analyzed by the AOCS Official Method Ce 8-89 (17) as described previously (1). Levels of tocopherols were quantified using separate calibration curves for α- and γ-tocopherol isomers.

Metal analysis. The amounts of Cu, Fe, and Ni in the fresh oil were determined following the AOCS Official Method Ca 18b-91 (18). The analyses were performed at the Grain Research Laboratory of the Canadian Grain Commission (Winnipeg, Canada).

Statistical analysis. The rates of TPC and FFA accumulation and tocopherol degradation were compared using analysis of covariance (ANCOVA) with frying time as the covariate variable. The model included the variables of specific oil type, frying time, and the interaction between them. ANCOVA was performed using SAS (Cary, NC) statistical software and allowed for the comparison of the rates (i.e., slopes). To compare rates between oils, *t*-tests were used for multiple comparisons.

RESULTS AND DISCUSSION

The initial quality of the sunflower oils is shown in Table 1. Both were found to have PV values <0.8 meq/kg and FFA values <0.03, indicative of good-quality oils (19).

The FA compositions of the two sunflower oils are summarized in Table 2. RSFO contained 18.7% oleic acid, 68.3% linoleic acid, and 1.2% linolenic acid. HOSFO contained much lower levels of linoleic acid (3.2%) and much higher levels of oleic acid (88.9%). In addition, there were just trace amounts linolenic acid in HOSFO compared to RSFO.

Tocopherols are important minor constituents in oils, acting as natural antioxidants by slowing the rate of oxidative degradation. RSFO had a much higher tocopherol content, 632 mg/kg, compared with 358 mg/kg for HOSFO (Table 3). The α-isomer was the predominant tocopherol present (94–96%); the γ-isomer accounted for only 2–3%. The importance of tocopherols as antioxidants suggests that oils containing higher levels would be expected to exhibit greater stability. In the case of RSFO, the level of total tocopherols was 43.3% higher than that in HOSFO. However, this difference was offset by the marked reduction in PUFA in HOSFO compared with RSFO.

TABLE 1
Quality Parameters of Fresh Sunflower Oils[a]

Oil	PV (meq/kg)	FFA (% oleic acid)
RSFO	0.6 ± 0.01	0.03 ± 0.01
HOSFO	0.7 ± 0.01	0.02 ± 0.01

[a]All values are the average of duplicates. RSFO, regular sunflower oil; HOSFO, high-oleic acid sunflower oil.

TABLE 2
FA Composition of Fresh Sunflower Oils[a]

Oil	SFA	PUFA	18:1	18:2	18:3
RSFO	11.2 ± 0.3	69.5 ± 0.2	18.7 ± 0.1	68.3 ± 0.2	1.2 ± 0.01
HOSFO	7.0 ± 0.22	3.6 ± 0.1	88.9 ± 0.1	3.2 ± 0.1	0.4 ± 0.02

[a]All values are the average of duplicate analyses. SFA, saturated FA; 18:1, oleic acid; 18:2, linoleic acid; 18:3, linolenic acid; for other abbreviations see Table 1.

TABLE 3
Tocopherol Content and Composition[a]

Oil	Tocopherols (mg/kg)	Tocopherol isomers (%) α	γ
RSFO	632 ± 50	94	3
HOSFO	358 ± 45	96	2

[a]All values are averages of duplicate analysis for total tocopherols. For abbreviations see Table 1.

TABLE 4
Tocopherol Degradation Rates[a,b]

Oil	Total tocopherols	α-Tocopherol	γ-Tocopherol
RSFO	12–24 (7.5)	12–24 (7)	12–24 (0.6)
HOSFO	0–3 (89.5)	0–3 (70)	0–3 (0.2)

[a]Time, in hours, required to reduce original levels by 50% (rate of degradation: ppm/h of frying time).
[b]All values are average of duplicate analyses. See Table 1 for abbreviations.

RSFO displayed markedly slower rates of degradation of total, α- and γ-tocopherols (12 to 24 h) during frying compared with HSFO (0 to 3 h). Thus, the total tocopherols in HOSFO degraded at substantially greater rates compared with RSFO (Table 4; Fig. 1).

The different rates of tocopherol degradation may explain, in part, the greater rate of formation of FFA observed for HOSFO compared with RSFO (Fig. 2). Warner *et al*. (20) found that the higher the oleic acid content of the oil was, the higher the FFA content in the heated oil. Likewise, in this study HSFO exhibited the faster rate of FFA accumulation (Fig. 2). However, Warner *et al.* (20) only heated the oil for18 h; they looked at the levels of FFA rather than rates of formation. They did not measure tocopherol levels.

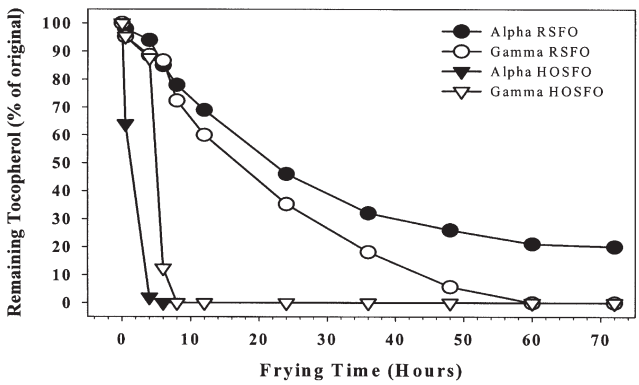

FIG. 1. Tocopherol changes during frying in regular sunflower oil (RSFO) and high-oleic acid sunflower oils (HOSFO).

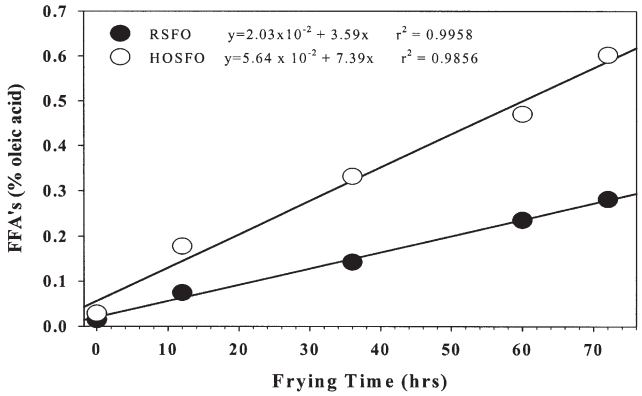

FIG. 2. Formation of FFA in RSFO and HOSFO during frying; for abbreviations see Figure 1.

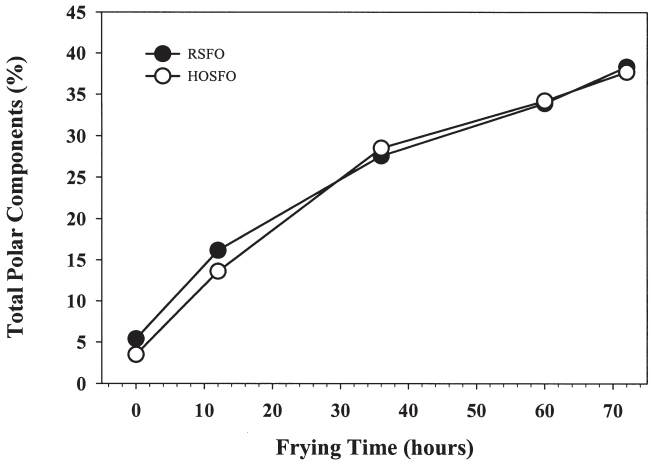

FIG. 3. Formation of polar components in RSFO and HOSFO during frying. For abbreviations see Figure 1.

A comparison of the rate of formation of TPC (Fig. 3), however, showed there were no significant differences between RSFO and HOSFO. In following the formation of different types of polar components, some small differences were observed (Figs. 4 and 5). RSFO produced 5% more polymeric components, whereas HOSFO produced more oxidized TG and TG dimers. The detection of both of these components indicated that oxidation was faster with HOSFO. The latter results were unexpected as HOSFO, with substantially lower levels of PUFA (3.5%), would be expected to show improved frying stability compared with RSFO having 67.5% PUFA. Thus, the combination of higher levels of tocopherols and their markedly slower rate of degradation in RSFO during frying probably provided greater protection to PUFA against oxidation. The presence of only trace amounts of avenasterol, a phytosterol antioxidant, in both RSFO and HOSFO eliminated its role in the frying behavior of these two oils. In addition, the absence of detectable amounts of Fe, Ni, and Cu (below the detection limit of 0.010 mg/kg) in both sunflower oils could not explain the differences in frying stability between these two oils.

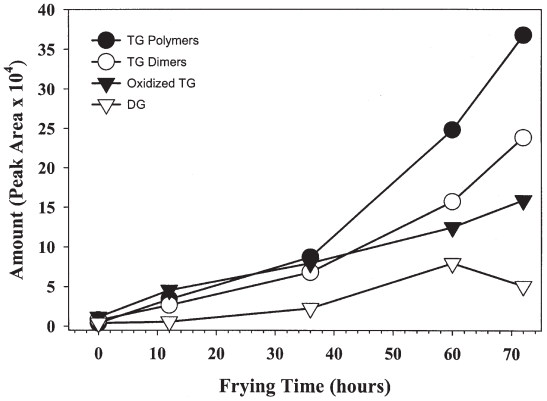

FIG. 4. Formation of TG degradation products in RSFO during frying. For abbreviation see Figure 1.

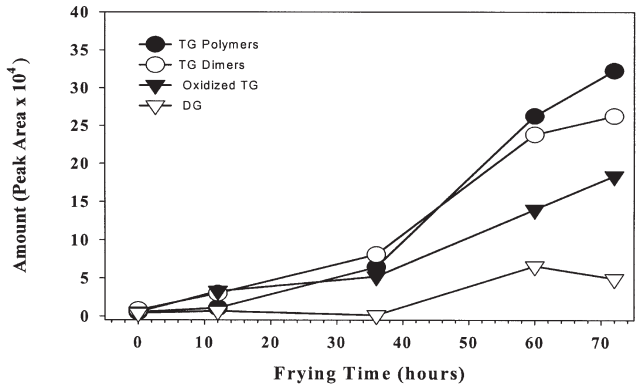

FIG. 5. Formation of TG degradation products in HOSFO during frying. For abbreviation see Figure 1.

Thus, the unexpected faster rate of FFA formation in HOSFO was attributed to lower level of tocopherols and their faster degradation compared with RSFO. The similar rates of TPC formation for HOSFO and RSFO could not be explained by the marked differences in FA composition between the two sunflower oils. The greater production of oxidized TG by HOSFO was also not expected based on the low level of PUFA in this oil compared with RSFO. Thus, plant breeders cannot ignore minor components in their effort to manipulate FA composition.

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