Frying Quality and Oxidative Stability of Two Unconventional Oils

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ABSTRACT: The behavior of crude *Sclerocarya birrea* kernel oil (SCO) and Sorghum bug (*Agonoscelis pubescens*) oil (SBO) during deep-frying of par-fried potatoes was studied with regard to chemical, physical, and sensory parameters, such as content of FFA, tocopherols, polar compounds, oligomer TG, volatile compounds, oxidative stability, and total oxidation (TOTOX) value. Palm olein was used for comparison. Whereas potatoes fried in SCO that had been used for 24 h of deep-frying at 175°C were still suitable for human consumption, potatoes prepared in SBO that had been used for 6 to 12 h were not, considering the sensory evaluation. In looking at the chemical and physical parameters, SBO exceeded the limits, after no later than 18 h of use, for the amount of polar compounds, oligomer TG, and FFA recommended by the German Society of Fat Sciences (DGF) as criteria for the rejection of used frying oils. In contrast to SBO, SCO oil did not exceed the limits for the content of polar compounds and oligomer TG during the frying experiment. Only the amount of FFA was exceeded; this was because the amount of FFA at the beginning of the experiment was higher than for refined oils. The results showed that both oils were suitable for deep-frying of potatoes, but remarkable differences in the time during which both oils produced palatable products were found.

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KEY WORDS: *Agonoscelis pubescens*, deep-fat frying, oxidative stability, *Sclerocarya birrea*.

Sclerocarya birrea subsp. *caffera* is a savannah tree belonging to the family Anacardiaceae. The common English name is Marula, and the tree is commonly known in Sudan as Homeid, where it is widely distributed in western and southern areas. The plant develops pale yellow plum-like fruits that are 3–4 cm in diameter with a plain, tough skin and a juicy, mucilaginous flesh. The fruit is edible and contains a hard brown seed. The seed encloses two or three soft white edible kernels (nuts), which are rich in oil and protein (1). These nuts have a high nutritive value resulting from the high protein and oil content (2). In the literature only a few reports dealing with the seed oil from *S. birrea* are available (3–6).

Agonoscelis pubescens (Sorghum bug) belongs to the order Hemiptera (family Pentatomidae), and is commonly known in Sudan as Dura andat. It is one of the main pests of sorghum (Dura) in both rain-fed and irrigated areas. Sorghum bug adults are collected and eaten after frying, and in some areas of Sudan the collected bugs are extracted and the obtained oil is used for cooking and some medicinal uses. In the Botana area of central Sudan, nomads use the tar obtained from highly heated bugs to treat their camels against dermatological infections.

Deep-fried foods and especially fried potatoes are becoming more and more popular, not only in industry but also in food services and at home. It is estimated that nearly one-half of all lunch and dinner food orders in commercial restaurants include one or more deep-fried items (7).

During deep-frying, oil is exposed to elevated temperatures in the presence of air and moisture. Under these conditions a number of chemical reactions occur, including oxidation, hydrolysis, and polymerization of unsaturated FA, that change the composition of the frying medium as well as produce volatile chain-scission products, nonvolatile oxidized derivatives, and dimeric, polymeric, or cyclic substances (8,9). Therefore, the oil quality as well as the composition of the oil is of great importance, since during deep-frying the oil becomes part of the food.

Przybylski *et al*. (10) showed that FA composition could account for only half of the storage and frying stability of vegetable oils. The other half was related to the content and composition of minor components such as tocopherols, sterols, and other compounds. Therefore, from a nutritional point of view the oils used for frying should on the one hand be low in PUFA, such as linoleic or linolenic acid, and high in oleic acid with moderate amounts of saturated FA, and on the other hand they should contain appropriate amounts of minor components for improving oxidative stability.

Since commonly used edible oils, such as groundnut or sesame, are less available in some rural parts of Sudan, oil sources such as *S. birrea* seeds or Sorghum bugs are important oil sources for the population. Earlier investigations showed that oil from seeds of *S. birrea* were distinguished by an extraordinarily high oxidative stability of more than 40 h at 120°C in the Rancimat test (6). From this it was obvious that the suitability of this oil for deep-frying, which is one of the most important and easiest methods for food preparation, should be tested.

The objective of this study was to investigate the suitability of two unconventional Sudanese oils, *S. birrea* oil (SCO) and

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Sorghum bug oil (SBO), for deep-fat frying in order to open an alternative oil source for areas where commonly used oils are not available.

MATERIALS AND METHODS

Materials. All solvents used were of analytical grade: *n*-hexane, *n*-heptane, isooctane, glacial, acetic acid, diethyl ether, petroleum ether, chloroform, ethanol, and methanol (Merck, Darmstadt, Germany). *p*-Anisidine and THF were from Sigma-Aldrich (Taufkirchen, Germany).

Samples. The oils for the frying experiment were obtained from *S. birrea* seeds and Sorghum bugs as follows.

Dried seeds of *S. birrea* were collected manually from Ghibaish and Abu Gibaiha provinces of western Sudan. Seeds were dehulled (decorticated) using a model 2XFRONT Heuer Vise (Heuer, Plettenburg, Germany), crushed, and ground by passage through a 0.5-mm sieve of a grinding mill (Petra Electric, Burgau, Germany). The oil was extracted from the ground material with diethyl ether in a Soxhlet apparatus for 6 h following the AOCS method (11). Solvent was removed by vacuum evaporation at 40°C for 1 h. The oil was stored at −4°C until it was used for frying.

Specimens of *A. pubescens* were collected from the Rahad Agricultural Project area in central Sudan. The bugs were stored in a tight polyethylene bag, killed by treatment with hot water for few minutes, and then sun dried. After crushing using a laboratory mortar and pestle, the oil was extracted using diethyl ether following the AOCS method (11). Solvent was removed by vacuum evaporation at 40°C for 1 h. The oil was stored at −4°C until it was used for frying.

Both oils were used for frying without further purification, such as refining.

Palm olein used for comparison was obtained from a German oil mill.

Frying procedure. An outline of the frying experiments is shown in Scheme 1. For each experiment 2 L of oil was put into an electric fryer (Oleoclean; Tefal, Rumilly, France) and heated to 175 ± 2°C within 10 min. After 1 h, 100 g of potatoes (8 × 8 mm in diameter and 10 cm long), par-fried in palm olein (Schne-Frost, Löningen, Germany) were introduced into the hot oil and fried for 7 min in SBO and 5 min in SCO, respectively. The different frying times of 5 and 7 min, respectively, were determined in preliminary tests of the optimal frying conditions for each oil. The oil was kept hot for 1 h before the next frying was carried out. Each day for 5 d, five batches of potatoes were fried within 6 h in the case of SBO and each day for 10 d for SCO. SCO was used only for 5 d, because the oil was no longer usable for deep-frying after that time. The total temperature load of the oils was 30 and 60 h, respectively, for SBO and SCO. At the end of each day the oil was cooled, 200 mL was removed from the fryer for the assessment of the oil, and this was stored at −4°C until the day of analysis. The fryer was cleaned without removing any adhering gum and topped up with 200 mL of fresh oil ready for the next trial.

Sensory evaluation of potatoes being fried. Trained panelists were chosen to taste the fried potatoes for the characterization of their organoleptic properties (color, flavor, and texture) after each batch was fried. For that, the Karlsruher organoleptic system (Germany) was used, which includes descriptive terms using numerical scores for each quality parameter starting from 9 = excellent to 1 = very bad. All analyses were done in triplicate, and the mean value was used.

Volatile compounds. Volatile compounds were determined by the method of dynamic headspace concentration. About 200 mg of oil was weighed exactly into a 20-mL headspace vial, sealed, and put into a PTA3000 (Axel Semrau, Sprockhövel, Germany) auto sampler. Volatiles were purged with nitrogen at 10 psi (6.9 kPa) with a stream of 20 mL/min over the sample surface at 80°C and trapped in an on-line Tenax trap (eightfold volume) at −65°C using carbon dioxide cooling. After 20 min of trapping, all volatiles were removed by heating the trap to 200°C for 10 min. The purge valve was held at 150°C and the transfer line (uncoated fused silica) at 200°C to avoid re-condensation without any water trap in the system. The heating jacket of the transfer line was connected to a split/splitless injector of a Hewlett-Packard model 5890 gas chromatograph instead of the septum cap and the transfer line was lead through the injector directly into the oven where it was connected to a guard column (CARBOWAX, (Varian, Palo Alto, CA) 1 m × 0.32 mm i.d. × 0.25 μm film thickness), and a Y-split to two separating columns: (i) CP-Sil 19 (Varian) (14% cyanopropylphenyl + 86% dimethylpolysiloxane, 60 m × 0.32 mm i.d. × 1 μm film thickness; (ii) CARBOWAX, 60 m × 0.32 mm i.d. × 1.2 μm film thickness. Both columns were connected to an FID at 280°C. The oven temperature was held for 5 min at 40°C, with no additional cold trap focusing necessary; 3°C/min to 245°C, and 10 min isothermal.

Polar compounds. The determination of the polar compounds was carried out according to the method DGF C-III 3b (12). In brief, 2.5 ± 0.1 g of the sample material was weighed into a 50-mL measuring flask and dissolved in a mixture of petroleum benzene and diethylether (87:13, vol/vol). Twenty milliliters of this solution was put onto a column of silica gel 60 (water content 5%; Merck), and the nonpolar compounds were eluted with 150 mL of a mixture of petroleum benzene and diethylether (87:13, vol/vol) into a weighed flask. The solvent was removed by rotary evaporation, and afterward the flask was dried to a constant weight at 103 ± 2°C. The content of polar compounds was calculated as the difference between the amount of oil used for the investigation and the amount of nonpolar compounds in the flask.

Oligomer TG. The content of oligomer TG was determined with gel-permeation chromatography by HPLC according to AOCS method Cd 22-91 (11). In brief, 0.1 g of the sample was dissolved in 2.5 mL THF. Of this, 20 μL was injected onto two coupled PLgel columns (5 μm, 100 Å, 300 × 7.5 mm; Polymer Laboratories, Darmstadt, Germany) tempered in a column oven (T-6300; Merck) at 35°C and used with a flow rate of 1.0 mL/min. The mobile phase consisted of THF puriss.; absolut, stabilized

with 0.025% 2,6-di-*tert*-butyl-*p*-cresol. The oligomer TG were detected by a refractive index detector (RI) (ERC 751, ERC, Riemerling, Germany) adjusted to 35°C. Margaric acid (0.5% in THF) was used for the determination of the retention time of FFA.

FFA. The amount of FFA was determined according to the method DGF C-V 2 (12). In brief, 3 to 10 g of the sample was dissolved in 50 mL of ethanol/diethylether (1:1, vol/vol) neutralized with 0.1 N potassium hydroxide solution against phenolphthalein. This solution was titrated with a 0.1 mol/L potassium hydroxide solution to the end point when the indicator (phenolphthalein) changed the color. The amount of FFA was expressed in g/100 g.

PV. PV was determined following the DGF method C-VI 6a (12). In brief, a 5-g sample was dissolved in 50 mL of a glacial acetic acid/isooctane (3:2) mixture and 0.5 mL of a saturated potassium iodide solution was added. The liberated iodine was then titrated with sodium thiosulfate. All analyses were done in triplicate and the mean value was used.

Anisidine value (AnV). The AnV was determined following the DGF method C-VI 6e (12). In brief, 0.5 to 4.0 g of the sample was dissolved in 25 mL of isooctane, and the absorbance of the solution was measured at 350 nm against isooctane. Then 5 mL isooctane was added to 5 mL of the fat solution and mixed with 1 mL of the *p*-anisidine reagent (0.25 g/100 mL glacial acetic acid). After 10 min, the absorbance was measured against isooctane. Additionally, a blank consisting of isooctane and *p*-anisidine solution was measured against isooctane. The AnV was calculated according to the formula given in the method.

Tocopherol. For determination of tocopherols, a solution of 250 mg oil in 25 mL *n*-heptane was used for HPLC. The HPLC analysis was conducted using a Merck-Hitachi low-pressure gradient system, fitted with a L-6000 pump, a Merck-Hitachi F-1000 fluorescence spectrophotometer (detector wavelengths for excitation 295 nm, for emission 330 nm), and a D-2500 integration system. Samples (20 μL) were injected by a Merck 655-A40 auto sampler onto a diol phase HPLC column (25 cm × 4.6 mm i.d.; Merck) using a flow rate of 1.3 mL/min. The mobile phase used was *n*-heptane/*tert*-butyl methyl ether (99:1, vol/vol) (13).

Oxidative stability (Rancimat method). The oxidative stability of the fried oils was determined by the Rancimat method (14). All experiments were carried out with a 743 Rancimat (Metrohm AG, Herisau, Switzerland). In brief, 3.6 g oil was weighed into the reaction vessel, which was placed into the heating block kept at 120°C. Air flow was set at 20 L/h for all determinations. Volatile compounds released during the degradation process were collected in a receiving flask filled with 60 mL of distilled water. The conductivity of this solution was measured and recorded. The software of the Rancimat system evaluated the resulting curves automatically. All determinations were carried out in duplicate.

Statistical analysis. The analyses were performed with three replicates. The mean values were calculated and tested using the Student *t*-test ($P > 0.05$). ANOVA was performed on all values using the statistical program Statgrafics® (Statistical Graphics System version 4.0) (15).

RESULTS AND DISCUSSION

The recommendations discussed and adopted by the delegates to the Third International Symposium on Deep-Fat Frying (March 20–21, 2000, Hagen/Westphalia, Germany) (16) pointed out that sensory evaluation is the most important parameter for the assessment of the quality of used frying oils, but for the analysis of suspect fats and oils the determination of polar compounds (>24%) and oligomer TG (>24%) should also be used. Many countries worldwide accept this approach. Additionally, the content of FFA (>2%) is used to verify the result of the sensory evaluation.

For these reasons, these parameters and limits were used for the evaluation of the two unconventional Sudanese oils during the frying experiment.

Sensory evaluation. The results of average scores obtained by the taste panel for the different oils are given in Table 1. For SCO, the color of the fried potatoes was evaluated as satisfactory by the taste panel during the frying experiment and no significant change was found. With respect to the softness and flavor of the potatoes, the results were only satisfactory during the first 24 h; afterward, the products being fried were not acceptable for human consumption and would be rejected by the consumer. A similar result was found for the crispness parameter. After only 12 h of frying, the crispness of the potatoes being fried was evaluated as being less than satisfactory. These results show that SCO was not suitable for deep-frying of potatoes beyond 24 h. Afterward, the products being fried were unacceptable from a sensory point of view, which results in a rejection of the products by the consumer.

In considering SBO, the results were more dramatic. Twelve hours of frying resulted in significant changes in the potatoes being fried. Although potatoes fried in SBO were evaluated as better than those fried in SCO within the first 6 h of frying, with progressive frying the quality of the potatoes fried with SBO rapidly worsened. This result was obtained not only for the flavor but also for color, crispness, and softness. Therefore, from a sensory point of view this oil was only suitable for about 6 h.

In comparison with palm olein, both oils were perceived as being less acceptable relative to the sensory evaluation. Whereas palm olein was suitable for deep -frying for more than 60 h, the acceptability of SCO and SBO was significantly lower ($P > 0.05$).

Volatile decomposition products. During deep-frying, volatile compounds are formed as a result of the degradation of the frying medium. These volatiles of vegetable oils have been extensively studied (17–19). Most of the volatile decomposition products, such as hydrocarbons, aldehydes, enals, dienals, ketones, and organic acids, are removed from the oil by the stream of water vapor generated during frying. Nevertheless, these compounds are of great interest, because some of these volatile products are retained in the fried food and greatly influence the

TABLE 1
Sensory Evaluation of French Fries, Fried in *Sclerocarya birrea* Oil (SCO), Sorghum Bug Oil (SBO), and Palm Olein at 175°C for 60 and 30 h, Respectively

Sample	Hours of frying	Sensory parameters[a,b,c]			
		Color	Flavor	Softness	Crispness
SCO	6	6.2[a]	6.0[a]	6.0[a]	6.0[a]
	12	6.0[a]	6.0[a]	6.0[a]	6.0[a]
	18	5.8[a]	6.0[a]	6.0[a]	5.4[b]
	24	6.0[a]	6.0[a]	6.0[a]	4.8[c]
	30	6.0[a]	5.4[b]	5.4[b]	4.8[c]
	36	6.0 [a]	5.4[b]	5.2[b]	4.4[c]
	42	6.0 [a]	4.2[c]	4.0[c]	4.2[c]
SBO	6	7.2[d]	7.2[d]	7.0[d]	7.0[d]
	12	5.4[b]	6.2[a]	5.0[b]	5.0[b]
	18	4.0[c]	4.4[c]	4.0[c]	4.0[c]
	24	3.6[e,c]	4.2[c]	3.2[e]	4.0[c]
	30	3.4[e,c]	4.2[c]	3.0[e]	3.0[e]
Palm olein	6	7.1[d]	7.6[d]	7.9[f,d]	8.0[f]
	12	7.3[d]	7.7[d]	7.9[f,d]	7.8[f,d]
	18	7.6[d]	7.4[d]	7.5[d]	7.7[d]
	24	7.5[d]	7.5[d]	7.8[d]	8.0[f]
	30	7.1[d]	7.6[d]	7.4[d]	7.3[d]
	36	7.3[d]	6.7[d,a]	6.1[a]	6.9[d]
	42	7.2[d]	6.6[d,a]	6.0[a]	6.3[a]
	48	6.8[d]	6.6[d,a]	5.7[a]	6.2[a]
	54	6.4[a]	6.6[d,a]	5.6[a]	6.3[a]
	60	6.3[a]	6.5[a]	5.7[a]	6.5[a]

[a]Where 9 = excellent to 1 = very bad.
[b]Mean of six observations.
[c]Means within a column followed by different superscripts are significantly different ($P > 0.05$).

aroma and the taste of the product (20). In addition, the short-chain components are very reactive and can react with other components of the food being fried, changing the composition and the taste of the food (21). They also may be inhaled by the deep-fryer operators and can have an effect on the health of these individuals. Since volatile compounds in frying oil are a result of the degradation of the oil, the development of volatile compounds shows a progressive degradation of the oil during use.

Volatiles (mg/kg oil) of SCO and SBO used for frying determined by dynamic headspace are listed in Tables 2 and 3. All of the volatiles found in this study are lipid oxidation products and have been reported in used frying oils in previous studies (19,21,22). The most predominant volatile compounds identified in both oils were *t*-2-nonenal, nonanal, decadienal, and *t*-2-decenal. In both oils, the amount of most of the volatile aldehydes increased significantly ($P < 0.05$) with increased frying time as a result of a degradation of FA due to the high temperature. The concentration of a few volatiles was reduced significantly ($P < 0.05$) with increasing frying time. One reason for this effect could be the behavior of unsaturated carbonyls and saturated carbonyls, which react differently with other compounds during the frying process and result in the reduction of the original component. That hypothesis coincides with results of Kiritsakis (17), who reported that both saturated and unsaturated carbonyls increased during olive oil oxidation and that the content of saturated carbonyl compounds increased faster than the unsaturated ones. The low levels of hexanal and pentanal are a result of the low to moderate level of linoleic acid in SCO and SBO, since these compounds are formed as degradation products of linoleic acid (19).

Polar compounds. The amount of polar compounds is one of the most reliable criteria for the assessment of frying oil quality for human consumption. Research has shown that the fraction of polar compounds isolated from oxidized oil is very toxic to laboratory animals (23). Therefore, according to the recommendations of the Third International Symposium on deep-fat frying in 2000 (16), in several European countries maximal values for polar compounds between 24 and 27% have been set for commercial used frying oils.

Figure 1 shows the results of the determination of polar compounds in the two oils during frying. Although the amount of polar compounds increased very fast for SBO during successive frying sets, a much more moderate increase of the polar compounds was found for SCO. Here the amount of polar compounds increased from 4.9% as initial value to 18.3% after 60 h of frying, which was below the limit of 24%, defined in Germany for the acceptable amount of polar compounds in used frying oils. Therefore, the oil was still suitable for human consumption. In the case of SBO the proportions were much different. The amount of polar compounds increased quickly from 8.2% as initial value to 26.8 after 24 hours of frying. This means that SBO exceeded the limit for polar compounds after only 24 h, leading to a rejection of the oil for human consumption. In comparison with palm olein, the increase of polar compounds in SCO was somewhat higher, but comparable.

TABLE 2
Development of Volatile Compounds (mg/kg oil) of Sorghum Bug Oil[a] During Frying at 175°C for 30 h

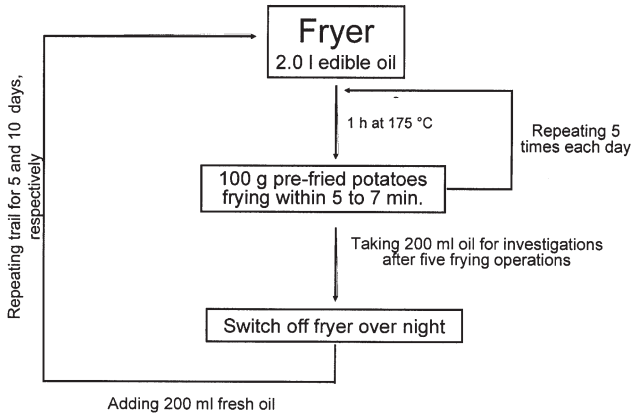
Hours of frying	Pentanal	Hexanal	Heptanal	t-2 hexenal	Octenal	t-2-heptenal	Nonanal	t-2-octenal	t-2-nonenal	t-2-decenal	t-2-undecenal	Decadienal
0	0.5 ± 0.2 ^{a}	1.0 ± 0.1^{a}	1.4 ± 0.1^{a}	0.4 ± 0.1^{a}	2.5 ± 0.2^{a}	5.2 ± 0.2^{a}	5.6 ± 0.3^{a}	3.8 ± 0.1^{a}	8.4 ± 0.3^{a}	3.2 ± 0.2^{a}	1.8 ± 0.1^{a}	1.9 ± 0.1^{a}
6	0.4 ± 0.1^{a}	1.5 ± 0.1^{a}	5.7 ± 0.2^{b}	0.8 ± 0.2^{b}	2.7 ± 0.3^{a}	1.6 ± 0.2^{b}	6.4 ± 0.3^{b}	2.4 ± 0.1^{b}	12.1 ± 0.3^{b}	15.2 ± 0.3^{b}	2.5 ± 0.2^{b}	3.5 ± 0.2^{b}
12	1.0 ± 0.2^{b}	2.4 ± 0.2^{b}	0.9 ± 0.2^{c}	1.2 ± 0.2^{b,c}	3.0 ± 0.2^{a}	2.2 ± 0.2^{c}	9.3 ± 0.5^{c}	3.5 ± 0.2^{a}	13.0 ± 0.3^{c}	2.9 ± 0.1^{a}	2.8± 0.1^{b}	4.0 ± 0.3^{b}
18	1.8 ± 0.3^{c}	0.5 ± 0.1^{c}	1.6 ± 0.2^{a}	1.5 ± 0.1^{c}	3.5 ± 0.3^{a,b}	3.4 ± 0.3^{d}	17.3 ± 0.6^{d}	6.9 ± 0.4^{c}	11.0 ± 0.2^{d}	4.5 ± 0.2^{c}	3.4 ± 0.2^{c}	8.3 ± 0.3^{c}
24	1.6 ± 0.3^{c}	0.4 ± 0.1^{c}	3.5 ± 0.1^{d}	1.7 ± 0.2^{c}	3.3 ± 0.1^{a,b}	2.3 ± 0.3^{c}	16.7 ± 0.3^{d}	6.6 ± 0.2^{c}	14.0 ± 0.1^{e}	5.0 ± 0.1^{d}	3.8 ± 0.2^{c}	7.9 ± 0.4^{c}
30	1.7 ± 0.4^{c}	0.4 ± 0.1^{c}	1.2 ± 0.2^{a}	2.3 ± 0.2^{d}	2.5 ± 0.3^{a}	2.4 ± 0.2^{c}	12.3 ± 0.3^{e}	6.2 ± 0.3^{c}	19.5 ± 0.2^{e}	5.7 ± 0.2^{e}	3.9 ± 0.2^{c}	7.1 ± 0.4^{c}

[a]Determinations were carried out in triplicate, and the mean values ± SD are reported. Means within a column followed by different superscripts are significantly different ($P < 0.05$).

TABLE 3
Development of Volatile Compounds[a] (mg/kg oil) of *Sclerocarya birrea* Oil During Frying at 175°C for 60 h

Hours of frying	Pentanal	Hexanal	Heptanal	t-2hexenal	Octenal	t-2-heptenal	Nonanal	t-2-octenal	t-2-nonenal	t-2-decenal	t-2-undecenal	Decadienal
0	0.8 ± 0.1^{a}	2.1 ± 0.3^{a}	1.2 ± 0.1^{a}	0.5 ± 0.1^{a}	2.0 ± 0.1^{a}	0.5 ± 0.1^{a}	8.7 ± 0.2^{a}	3.2 ± 0.1^{a}	5.8 ± 0.4^{a}	2.0 ± 0.2^{a}	2.1 ± 0.2^{a}	2.9 ± 0.2^{a}
6	1.2 ± 0.2^{b}	0.6 ± 0.1^{b}	0.7 ± 0.1^{b}	3.1 ± 0.2^{b}	3.2 ± 0.2^{b}	0.9 ± 0.2^{b}	10.8 ± 0.4^{b}	4.6 ± 0.2^{b}	7.9 ± 0.3^{b}	3.9 ± 0.3^{b}	2.5 ± 0.1^{b}	3.4 ± 0.3^{b}
12	1.1 ± 0.1^{b}	0.9 ± 0.1^{b}	0.8 ± 0.2^{b}	3.0 ± 0.3^{b}	3.1 ± 0.2^{b}	1.1 ± 0.2^{b}	11.7 ± 0.3^{c}	5.1 ± 0.3^{b}	9.3 ± 0.4^{c}	4.9 ± 0.2^{c}	2.9 ± 0.2^{c}	3.4 ± 0.2^{b}
18	3.5 ± 0.2^{c}	1.1 ± 0.2^{bc}	0.9 ± 0.2^{b}	3.1 ± 0.2^{b}	3.3 ± 0.2^{b}	1.2 ± 0.1^{b}	11.9 ± 0.2^{c}	5.8 ± 0.2^{c}	10.4 ± 0.2^{d}	6.0 ± 0.0^{d}	3.4 ± 0.1^{d}	3.4 ± 0.3^{b}
24	3.4 ± 0.2^{c}	1.1 ± 0.2^{b,c}	0.9 ± 0.2^{b}	3.2 ± 0.3^{b}	3.3 ± 0.1^{b}	1.1 ± 0.1^{b}	11.8 ± 0.5^{c}	6.3 ± 0.2^{c}	10.9 ± 0.3^{d}	6.6 ± 0.0^{d}	3.9 ± 0.3^{e}	3.6 ± 0.4^{b,c}
30	0.4 ± 0.1^{d}	1.4 ± 0.1^{c}	1.2 ± 0.1^{b,c}	3.9 ± 0.3^{c}	4.0 ± 0.3^{c}	1.3 ± 0.1^{b,c}	13.4 ± 0.6^{d}	7.3 ± 0.3^{d}	12.1 ± 0.3^{e}	7.3 ± 0.2^{e}	4.1 ± 0.3^{e}	4.1 ± 0.3^{c}
36	0.4 ± 0.1^{d}	1.3 ± 0.2^{c}	1.2 ± 0.1^{b,c}	3.5 ± 0.1^{b,c}	3.9 ± 0.3^{c}	1.2 ± 0.2^{b}	12.9 ± 0.4^{d}	7.1 ± 0.3^{d}	12.4 ± 0.4^{e}	7.5 ± 0.3^{e}	4.3 ± 0.3^{f,g}	4.6 ± 0.5^{c}
42	0.4 ± 0.1^{d}	1.2 ± 0.2^{c}	1.1 ± 0.2^{b,c}	3.0 ± 0.1^{b}	3.8 ± 0.2^{c}	1.1 ± 0.2^{b}	12.1 ± 0.3^{c}	7.0 ± 0.1^{d}	12.7 ± 0.2^{e,f}	7.3 ± 0.4^{d}	4.6 ± 0.3^{f}	4.0 ± 0.4^{c}
48	0.5 ± 0.1^{d}	1.5 ± 0.2^{c,d}	1.4 ± 0.1^{c}	3.6 ± 0.2^{c}	4.4 ± 0.3^{c,d}	1.3 ± 0.2^{b,c}	13.9 ± 0.5^{d,e}	8.3 ± 0.2^{e}	13.3 ± 0.5^{f}	7.8 ± 0.3^{e,f}	4.9 ± 0.2^{f}	4.5 ± 0.5^{c}
54	0.4 ± 0.1^{d}	1.3 ± 0.1^{c}	1.3 ± 0.2^{c}	3.4 ± 0.2^{b,c}	4.3 ± 0.3^{c,d}	1.2 ± 0.1^{b}	14.5 ± 0.2^{e}	8.4 ± 0.3^{e}	14.1 ± 0.4^{f}	7.7 ± 0.2^{f}	4.9 ± 0.4^{f}	3.3 ± 0.4^{b}
60	0.5 ± 0.1^{d}	1.6 ± 0.1^{d}	1.5 ± 0.1^{c}	3.8 ± 0.3^{c}	5.1 ± 0.2^{e}	1.3 ± 0.1^{b,c}	17.3 ± 0.2^{f}	10.3 ± 0.5^{f}	18.5 ± 0.3^{g}	9.4 ± 0.4^{g}	6.4 ± 0.3^{h}	4.5 ± 0.5^{c}

[a]Determinations were carried out in triplicate, and the mean value ± SD is reported. Means within a column followed by different subscripts are significantly different ($P < 0.05$).



SCHEME 1

Oligomer TG. Another reliable method for the assessment of used frying fats and oils is the determination of the oligomer TG, which has been recognized worldwide as one of the most suitable methods for monitoring the degree of degradation of used frying fats and oils (24).

In the recommendations of the German Society of Fat Sciences a limit of 12% oligomer TG is established for the assessment of used frying fats and oils (16).

As expected, both oils showed increasing contents of oligomer TG with increasing frying time. Whereas in SCO oligomer TG increased only from 0.39 to 3.42% within 60 h of frying, which was well below the limit of 12%, the increase was more notable for SBO (6.1 to 14.2%) within 30 h of frying (Fig. 2). Already after 24 h of frying, SBO was no longer suitable for frying of human food. The increase of oligomer TG in SCO was comparable to that in palm olein.

FFA. Another parameter often used for the assessment of the suitability of used frying fats and oil for human consumption is the content of FFA. Here a value of 2% is defined as the limit, before the oil has to be rejected (16).

The changes in FFA level of the two oils during frying are presented in Figure 3.The FFA of SCO increased gradually from an initial value of 1.5% to 4.2% after 60 h of frying. This increase was not linear with the frying time, because in the first 30 h the increase was more rapid than at the end of the frying experiment, where the development of FFA was only very slight.

In the case of SBO the FFA levels increased from 9.3% to 11.3% after 24 h of frying.

At the beginning of the frying experiment, SCO was barely below and SBO was above the limit of 2% FFA. Therefore, it was not surprising that both oils quickly exceeded the limit for FFA. One reason for the high initial content of FFA was that the oil was processed without a refining step to improve the quality of the oil.

In comparison, the development of FFA in palm olein was only slight. After 60 h of frying the amount was still below 2%.

TOTOX value. The TOTOX value is defined as the sum of 2 × PV + AnV. This means that the TOTOX value not only describes the state of the oil with regard to the amount of peroxides but also considers the formation of decomposition products of the oxidation process. Using only the PV is problematic because peroxides are destroyed by high temperatures during the frying process and new peroxides are formed during cooling (25). Therefore, Fritsch (26) stated that the determination of PV is not suitable for the assessment of used frying oils.

In the present investigation, after 30 (SBO) and 60 h (SCO), the PV of the two oils was below or only just below the limit of 10 mequiv O_2/kg (data not presented), given by the Guidelines of the German Food Codex as the limit for edible fats and oils. Therefore, deterioration of oils cannot be assessed properly by using PV alone.

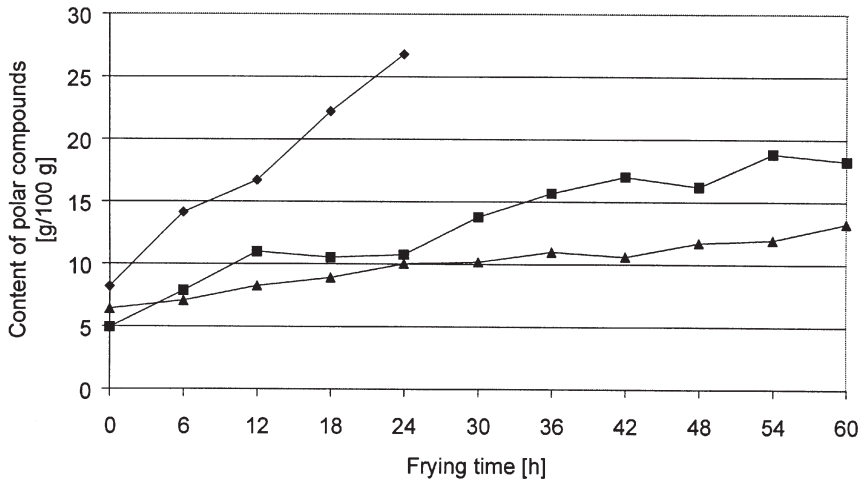


FIG. 1. Development of the content of polar compounds in *Sclerocarya birrea* oil (■), Sorghum bug oil (◆), and palm olein (▲) during frying of prefried potatoes at 175°C.

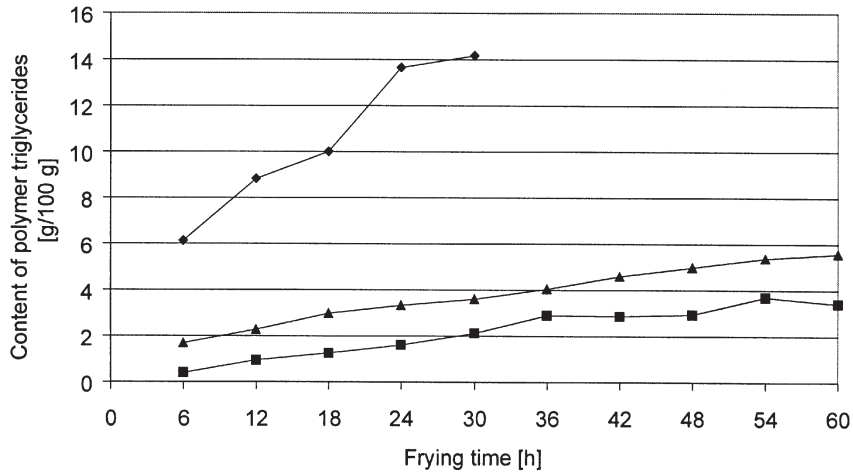


FIG. 2. Development of oligomer TG in *Sclerocarya birrea* oil (■), Sorghum bug oil (◆), and palm olein (▲), used for frying of prefried potatoes at 175°C.

In contrast to PV, the AnV does not measure primary products of the oxidation process, but rather secondary decomposition products such as carbonyl compounds (aldehydes and ketones). During frying, AnV changes much more than PV so that in frying AnV is the predominant value for the calculation of the TOTOX value (23). Therefore, the TOTOX value is more suitable for describing the oxidative degradation of the oil, since it takes into consideration both primary and secondary oxidation products.

For the industrial evaluation of oils and fats, the following classification has been made: High-quality refined oils show TOTOX values between 2 and 9, but even oils with TOTOX numbers between 10 and 30 are still acceptable for human consumption. Only oils with a TOTOX value higher than 32 should be rejected.

The results obtained in this study are shown in Figure 4. For SCO, only a very moderate increase of the TOTOX value was obtained. During 60 h of frying, the TOTOX value increased from about 1 to 30. In contrast, for SBO the increase of the TOTOX value was much more pronounced. At the beginning of frying, the TOTOX value already was near the limit of 32 for this oil, and after 30 h of frying the TOTOX value increased to a value exceeding 100. This means that, according to TOTOX value, SBO has to be rejected after 12 h of use, whereas SCO would be judged as acceptable for human consumption after 60 h of frying. In considering palm olein, this oil also shows much higher TOTOX values than SCO. In the first 12 h of frying, the TOTOX value of palm olein increased very fast and reached a maximum value of about 60, after which the TOTOX value remained nearly constant. The development of the TOTOX value of palm olein was comparable to that of SCO, where an intense increase of the TOTOX value was found in the first hours of frying

Tocopherol content. Tocopherols are natural antioxidants

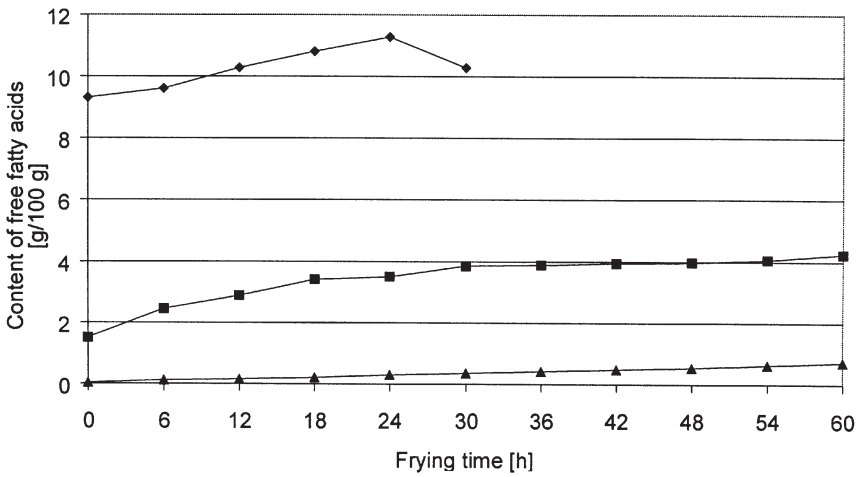


FIG. 3. Changes in FFA (%) in *Sclerocarya birrea* oil (■), Sorghum bug oil (◆), and palm olein (▲) used for frying of prefried potatoes at 175°C.

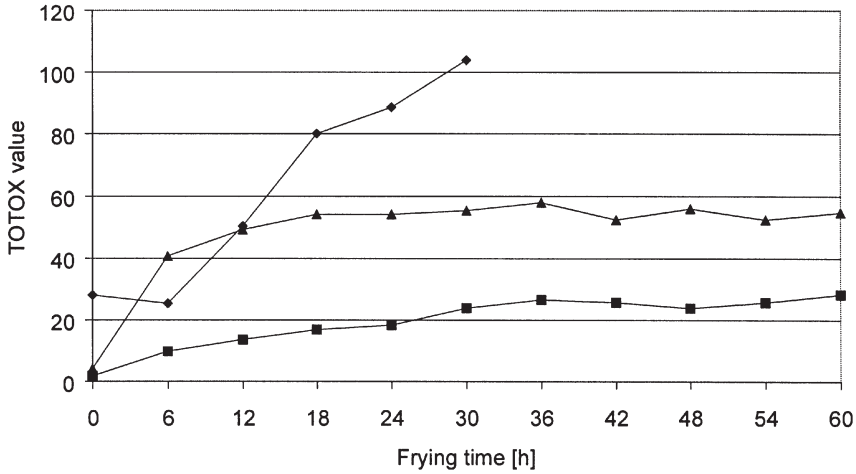


FIG. 4. Development of the TOTOX values in *Sclerocarya birrea* oil (■), Sorghum bug oil (◆), and palm olein (▲) used for frying of prefried potatoes at 175°C.

that are present in all vegetable oils in different amounts. During heating, rapid losses of tocopherols take place and such losses may be used as a measure to monitor the deterioration of frying oils (27).

Tables 4 and 5 illustrate the decrease in the amounts of individual tocopherols as well as of the total tocopherol content of SCO and SBO with increasing frying time. Within 18 h (SBO) and 24 h (SCO), more than 95% of the initial amount of tocopherols was degraded. In spite of the higher amount of total tocopherols at the beginning of the frying experiment, the degradation of tocopherols occurred significantly faster in SBO than in SCO, ($P < 0.05$) where 10% of the initial tocopherols were still available after 18 h. It is possible that, in addition to the tocopherols, SCO contains other antioxidative active components that retard the degradation of the tocopherols and increase the shelf life of the oil. It is known that SCO shows a high oxidative stability, which cannot be the result of only the FA or tocopherol composition (10). Therefore the presence of other compounds is possible.

In considering individual tocopherols, only the content of γ-tocopherol seems pertinent, because it constituted nearly 95% of the total amount of tocopherols in both oils. In SCO within the first 24 h and in SBO within the first 18 h of frying, almost all γ-tocopherol was lost. The degradation of α-tocopherol was equally fast, although the initial amount of α-tocopherol was lower. Although no α-tocopherol was detectable in SCO after the first 6 h of frying, in SBO a very low amount of α-tocopherol was found after 24 h.

Oxidative stability. The time that elapses until the oxidation process becomes very rapid is a useful measure to determine the resistance against oxidation, or oxidative stability (28) (also known as the induction period). The development of oxidative stability as measured by the Rancimat test is a useful screening method to follow the deterioration of oil during continuous frying (29). In contrast to the PV, which provides a static measure for the assessment of frying fats and oils, the determination of the oxidative stability by the Rancimat method is a dynamic measurement. In using this method, it is possible to compare

TABLE 4
Decrease of the Tocopherol Content[a] (mg/100 g) of *Sclerocarya birrea* Oil During Frying at 175°C for 60 h

Hours of frying	α-Tocopherol	γ-Tocopherol	δ-Tocopherol	Total
0	0.4 ± 0.1^{a}	13.2 ± 0.2^{a}	0.3 ± 0.1^{a}	13.7 ± 0.3^{a}
6	0.0 ± 0.1^{b}	7.0 ± 0.3^{b}	0.3 ± 0.1^{a}	7.3 ± 0.3^{b}
12	0.0 ± 0.0^{b}	1.8 ± 0.2^{c}	0.3 ± 0.1^{a}	2.0 ± 0.2^{c}
18	0.0 ± 0.0^{b}	0.9 ± 0.1^{d}	0.3 ± 0.1^{a}	1.1 ± 0.2^{d}
24	0.0 ± 0.0^{b}	0.5 ± 0.1^{e}	0.2 ± 0.1^{a}	0.7 ± 0.1^{e}
30	0.0 ± 0.0^{b}	0.3 ± 0.1^{f}	0.2 ± 0.1^{a,b}	0.4 ± 0.2^{e,f}
36	0.0 ± 0.0^{b}	0.3 ± 0.1^{f}	0.2 ± 0.1^{a,b}	0.4 ± 0.1^{e,f}
42	0.0 ± 0.0^{b}	0.3 ± 0.1^{f}	0.2 ± 0.1^{a,b}	0.4 ± 0.1^{e,f}
48	0.0 ± 0.0^{b}	0.2 ± 0.2^{f,g}	0.1 ± 0.1^{b}	0.4 ± 0.2^{e,f}
54	0.0 ± 0.0^{b}	0.2 ± 0.1^{f,g}	0.0 ± 0.0^{b}	0.2 ± 0.1^{f}
60	0.0 ± 0.0^{b}	0.1 ± 0.1^{g}	0.0 ± 0.0^{b}	0.1 ± 0.1^{f}

[a]Determinations were carried out in triplicate, and the mean value ± SD is reported. Means within a column followed by different superscripts are significantly different ($P < 0.05$).

TABLE 5
Decrease of the Tocopherol Content[a] (mg/100 g) of Sorghum Bug Oil During Frying at 175°C for 30 h

Hours of frying	α-Tocopherol	γ-Tocopherol	Plasto-chromanol-8	δ-Tocopherol	Total
0	0.9 ± 0.1[a]	32.2 ± 0.4[a]	0.2 ± 0.1[a]	0.8 ± 0.1[a]	34.0 ± 0.3[a]
6	0.7 ± 0.1[a]	12.7 ± 0.3[b]	0.0 ± 0.0[b]	0.0 ± 0.0[b]	13.4 ± 0.2[b]
12	0.3 ± 0.2[b]	3.4 ± 0.2[c]	0.0 ± 0.0[b]	0.0 ± 0.0[b]	3.7 ± 0.4[c]
18	0.1 ± 0.1[b]	0.0 ± 0.0[d]	0.0 ± 0.0[b]	0.0 ± 0.0[b]	0.1 ± 0.1[d]
24	0.1 ± 0.1[b]	0.0 ± 0.0[d]	0.0 ± 0.0[b]	0.0 ± 0.0[b]	0.1 ± 0.1[d]
30	0.0 ± 0.0[b]	0.0 ± 0.0[d]	0.0 ± 0.0[b]	0.0 ± 0.0[b]	0.0 ± 0.0[d]

[a]Determinations were carried out in triplicate, and the mean value ± SD is reported. Means within a column followed by different superscripts are significantly different ($P < 0.05$).

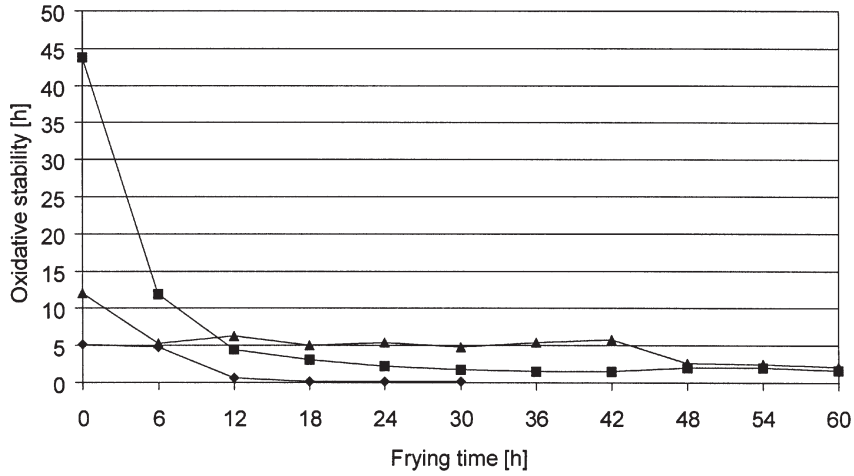


FIG. 5. Development of the oxidative stability of *Sclerocarya birrea* oil (■), Sorghum bug oil (◆), and palm olein (▲) used for frying of prefried potatoes at 175°C.

the degree of deterioration of oils resulting from the deep-frying process.

The oxidative stability of used frying oils decreased rapidly with increasing frying time (Fig. 5). This decrease was much more pronounced for SCO, which had a very high oxidative stability at the beginning of the experiment. After 6 h of frying, the oxidative stability of SCO was reduced to about 26% of the initial stability, and after an additional 24 h, a stability of about 1 h at 120°C in the Rancimat was measured, corresponding to about 3% of the stability at the beginning of frying. For SBO the results were somewhat different. In the first 6 h the oxidative stability decreased only about 6% and after a further 6 h the oxidative stability was far below 1 h, corresponding to a decrease of more than 95% within the first 12 h. In comparison, within the first 6 h of frying, the oxidative stability of palm olein was halved and afterward the decrease was comparable to that of SCO. After 60 h of frying the oxidative stability of palm olein was about 1 h.

This frying experiment showed that SCO was suitable for deep-frying of potatoes for at least 24 h. Considering the most important parameters for the assessment of used frying oils—sensory evaluation as well as contents of polar compounds, oligomer TG, and FFA—only the limit for FFA recommended by the Third International Symposium on Deep-fat Frying in 2000 was exceeded. The results for SCO are comparable to or only a little worse than for refined palm olein. In contrast to SCO, SBO was suitable for deep-frying only for 6 to 12 h. After that, the oil and the potatoes fried in it did not meet the requirements with regard to the sensory assessment or chemical parameters.

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