Improving the Oxidative Stability of Sunflower Oil by Blending with *Sclerocarya birrea* and *Aspongopus viduatus* Oils

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ABSTRACT
The paper describes the improvement of the oxidative stability of sunflower kernel oil (SKO) by blending with high stable unconventional edible Sudanese oils. Blends (9:1, 8:2, 7:3, 6:4 w/w) of sunflower oil with Sclerocarya *(Sclerocarya birrea)* oil (SCO) *and* melon bug (*Aspongopus viduatus)* oil (MBO), respectively, were studied with respect to the fatty acid composition, the oxidative stability (Rancimat 120°C) and the stability at 70°C evaluated by the development of the peroxide value. With increasing parts of SCO and MBO in SKO, the content of linoleic acid decreased from 46.3 to 31.2 % (SCO) and to 30.1 % (MBO), respectively, while the content of oleic acid increased from 41.3 to 51.0 % (SCO) and to 43.9 % (MBO), respectively. As a result of blending SKO with SCO and MBO, respectively, the oxidative stability in the Rancimat test was improved from 47 to 147% in (SCO) and from 5 – 68 % (MBO) compared to the sunflower kernel oil as control, with increasing parts of SCO and MBO, respectively. Storage of the blends at 70 °C showed that the increase of the peroxide value as measure for the oxidative deterioration was remarkable lower for the mixtures of MBO and SCO with SKO than for pure SKO. The study demonstrates a way to improve the stability of sunflower oil by blending with *Sclerocarya birrea* and *Aspongopus viduatus* oils.

INTRODUCTION

Sclerocarya birrea subsp. caffera is a Savannah tree, belonging to the family Anacardiaceae. The plant develops pale yellow fruits, which are plum-like, 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 2 - 3 soft white edible kernels (nuts), which are rich in oil and protein (FAO 1988, Mizrahi *et al.* 1996). The seeds named as "the kings nut" are highly appreciated by the local population, which eat them as delicate nuts. In literature only few reports dealing with the seed oil of *Sclerocarya birrea* are available (Salama 1973, Ogbobe 1992)

Aspongubus viduatus (melon bug) is a bug of 20 mm height, belonging to the order *Hemiptera*, whose members are called as "true bugs". Melon bugs are widely distributed in Sudan, mainly in western areas (Kordofan and Darfor states), where field watermelons are considered as one of the most important crops for the traditional rainfed agriculture. For small farmers of these states watermelons are strategic crops, due to the multipurpose uses, from the application as main source for drinking water during summer months in some remote areas to the application of the fruits residues in animal nutrition. In the western Kordofan state of Sudan the bug is known locally as Um-buga and used in nutrition by collecting the oil from the bugs after hot water extraction. The oil is used in cooking (during famine and shortage of food) and some medicinal applications e.g. skin lesion remedy.

In remote territories of Sudan oil from these bugs is used as sweet-oil. A poisonous effect of this oil is not described and the fatty acid composition corresponds with most animal oils (Tauscher *et al*.1981).
Apart from its nutritional function, fat contributes to the palatability of food and serves as an important cooking medium. In developed countries fats and oils contribute to about 40 – 45 % of the energy intake, but in developing countries this part comes to only 10 – 20% (Prakash *et al.* 2001).

The main edible oils consumed in Sudan are groundnut, cottonseed, sesame and sunflower oil. Blending with oils high in oxidative stability and rich in natural antioxidants can enrich these oils. Oxidative stability is an important parameter evaluating the quality of oils and fats, as it gives a good estimation of their susceptibility to oxidative deterioration, the main cause of their alteration.

Previous unpublished data revealed that *Sclerocarya birrea* and *Aspongopus viduatus* oils were high in oxidative stability (43 and 38 hr induction period, respectively; using Rancimat apparatus with 20 L/h air flow , and 120°C), in spite of their low content of tocopherols and sterols. Compared to 16-25 h (8-12.5 hr recalculated to 120°C) with 15 L/h air flow, and 110°C for hazelnut cultivars (Savage *et al* 1997) and 45-77 h (11-19 hr recalculated to 120°C) with 10 L/h air flow, and 100°C for virgin olive oil samples (Aparicio *et al* 1999). Data on *Sclerocarya birrea* and *Aspongopus viduatus* oils are rather limited .The objective of this study was to shed light on the oxidative stability of these oils and to improve the stability of sunflower oil by blending with different percentages of both *Sclerocarya birrea* and *Aspongopus viduatus* oils.

MATERIALS AND METHOD

Materials

Sunflower kernel oil was obtained from a local market.
All solvents used were of analytical grade: *n-hexane*, *n-heptane*, diethyl ether, ethanol and methanol (Merck, Darmstadt, Germany).

Dried seeds of *Sclerocarya birrea* were collected manually from Ghibaish and Abu Gibaiha provinces of western Sudan. Seeds were dehulled (decorticated) using a Vice model 2XFRONT equipment (Heuer, Germany), crushed and ground to pass through 0.5 mm sieve by a grinding mill, (Petra electric, Burgau, Germany). The oil was extracted from the ground material by extraction with n-hexane (b.p 50-60°C) in a Soxhlet apparatus for 6 hr. following the AOCS method Aa 4-38 (Official methods, AOCS 1993). Calculated percentages of 10, 20, 30, and 40% of SCO were added to SKO and the blends were mixed for 10 min. at room temperature using ultrasconic (Bandelin electronic, Berlin, Germany).

A. Viduatus was collected from Ghibaish province of western Sudan, and the oil was obtained by using a local hot water extraction method. In brief, the collected bugs were killed by a sudden hot water shock and crushed using a local woody mortar. The oil was extracted by using boiling water, and the top oily layer was collected. Then the oil was heated again to remove water drops and afterwards kept in a plastic container at 4 °C until further use. Calculated percentages of 10, 20, 30, and 40 % of MBO were added to SKO and the blends were mixed for 10 min. at room temperature using ultrasonic (Bandelin electronic, Berlin, Germany).

Fatty acid analysis: The fatty acid composition of SKO, SCO and MBO as the basic oils and their blends was determined following the method ISO 5509:1997. In brief, one drop of the oil was dissolved in 1 ml of n-heptane, 50 µl 2M sodium methanolate in methanol were added, and the closed tube was agitated vigorously for 1 min. After addition of 100 µL of water, the tube was centrifuged at 4500 g for 10 min. and the lower aqueous phase was removed. After adding 50 µL 1 M HCl to the heptane phase, the two phases were shortly mixed and the lower aqueous phase was rejected. About 20 mg of sodium hydrogen sulphate (monohydrate, extra pure, Merck, Darmstadt, Germany) were added, and after centrifugation at 4500 g for 10 min. the top n-heptane phase was transferred into a vial and injected into a Varian 5890 gas chromatograph equipped with a capillary column, CP-Sil 88 (100 m long, 0.25 mm ID, film thickness 0.2 µm). The temperature programme was: from 155 °C heated to 220 °C (1.5 C/min.), 10 min isotherm; injector 250°C, detector 250 °C; carrier gas 1.07 ml/min hydrogen; split ratio 1:50; detector gas 30 ml/min hydrogen; 300 ml/min air and 30 ml/min nitrogen; manual injection volume less than 1 µL. The peak areas were computed by integration software and percentages of fatty acid methyl esters (FAME) were obtained as weight percent by direct internal normalisation. All analyses were done in triplicate.

Oxidation*:* Samples (50 g) weighed into 250-ml Erlenmeyer flasks were oxidised at 70°C in the dark in a shaker water bath (Kottermann, Hänigsen Germany). A control sample consisting of SKO and SKO with BHA (0.02%) was prepared under the same conditions for comparison. The oxidative stability was evaluated by analysing the peroxide value (PV) of the oil samples periodically after 2, 4, 24, 32, 48, 56 and 72 hours. All analyses were done in duplicate.

Peroxide value

Peroxide value was determined following the German Society for Fat Science (Deutschen Gesellschaft für Fettwissenschaft) DGF method C-II 1 (DFG, 1994). All analyses were done in triplicate and the obtained mean value was used.

Oxidative stability (Rancimat method)

The oxidative stability of the basic oils and the blends was determined by the Rancimat method (Metrohm 1994). 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 distilled water. The conductivity of this solution was measured and recorded. The software of the Rancimat evaluated the resulting curves automatically. All determinations were carried out in duplicate.

Results and Discussions

The fatty acid composition of oils and blends is presented in table 1. The main fatty acids in the oils were linoleic, oleic, and palmitic acid with 46.3, 41.3, 5.7 % (SKO), 5.9, 68.0 and 14.2 % (SCO) and 3.9, 47.1, and 30.9 % (MBO), respectively (Table 1). Blending of SKO by 40 % SCO resulted in an increase of oleic acid from 41.3 to 51.0 % and a decrease of linoleic acid from 46.3 to 31.2 % in the mixture. The increase of saturated fatty acids as a result of blending SKO with SCO was only very small (10 to 14 %).

Frankel et al (1994) reported that mixtures of canola oil and high oleic sunflower oil containing 1.0 and 2.0 % linolenate are comparable or better in oxidative stability than the hydrogenated canola oil containing 1% linolenate, while Millwalla *et al*. (1986) showed that the measurements of iodine number and linoleic acid content indicated that blending sesame oil with cottonseed, safflower, or peanut oil improves the oxidative stability at 180°C.

The effect on the fatty acid composition by blending SKO with MBO was not as marked as blending with SCO. There was a small increase in the content of oleic acid (41.8 to 43.9 %) and a more pronounced decrease of linoleic acid (42.5 to 30.1 %). While the amount of stearic acid was not changed by blending with MBO, the content of palmitic acid increased from 8.1 to 15.4 %.

Rancimat and peroxide value were used to measure the oxidative stability of the blends in comparison to pure sunflower oil. BHA was used as standard antioxidant at a concentration of 0.02% to compare the effect on the oxidative stability as a result of adding unusual Sudanese oils to sunflower oil.

The oxidative stability measured by Rancimat at 120°C of SKO and its blends with SCO and MBO is shown in Table 2. Pure SKO showed an oxidative stability (induction period, IP) of about 1.9 h at 120 °C in the Ranicmat, whereas the stability of SCO and MBO was 43 and 38 h, respectively. A blending of SKO with the unusual Sudanese oils resulted in a remarkable increase of the oxidative stability from 1.9 to 4.7 h (SCO) and 1.9 to 3.2 h (MBO), which corresponds to an improvement of the oxidative stability of 147 and 68 %, respectively, for blends with 60 % SKO and 40 % unusual Sudanese oils.

In comparison, the addition of 0.02 % BHA to pure SKO resulted in an improvement of the oxidative stability from 1.9 h to 2.3 h, which corresponds to an increase of the oxidative stability of about 21 %. However, it should be taken into consideration that under the conditions of the Rancimat BHA is volatile; therefore its antioxidative activity at higher temperatures is not very marked. Nevertheless, a part of 10 % unusual Sudanese oils showed a similar effect on the oxidative stability of SKO in the Rancimat test as the addition of 0.02 % BHA.

For blends of SKO with MBO the improvement of the oxidative stability is not as good as for SCO Table 2 shows that the oxidative stability of SKO, blended with 10, 20, 30 and 40 % of MBO, respectively, is increased from 5 to 68 %.

Similar effects of blending on the improvement of the oxidative stability of edible oils were shown by Allam *et al.* (2001), who studied the oxidative stability of sunflower oil blended with nine oils

distinguished by their high oleic acid content. The results revealed a good correlation between the content of oleic acid and the oxidative stability of oils. The stability of sunflower oil increased with increasing amounts of oleic acid. Monika *et al*. (2002) reported that the oxidative stability of 1:1 rapeseed /palm olein blends was improved up to 60% in comparison to rapeseed oil, while Shiota *et al. (*1999) observed an improved oxidative stability of fish oil blended with butter.

Another method to compare the oxidative stability of the different blends is the storage under accelerated conditions at 70 °C and measurement of the peroxide value at certain times. Figure 1 shows the effect of different blends of SKO and SCO on the development of the peroxide value during storage of the oil at 70 C. Even an addition of 10 % SCO resulted in a remarkable improvement of the oxidative stability in comparison to pure SKO. Increasing amounts of SCO in the blend led to a drastical increase of the stability, and a mixture of 30 % SCO in the blend showed nearly no increase of the peroxide value during storage for 120 h at 70°C.

Looking at the mixtures with MBO (Fig 2) it is obvious that the effect of these blends is not as pronounced as for SCO. The different mixtures also show a remarkable effect on the improvement of the oxidative stability of the oils in comparison to pure SKO, but the peroxide value increased much faster compared to SCO. Under these storage conditions also BHA showed a remarkable antioxidant activity and the figure demonstrates that the addition of 30 % MBO and especially of 40 % MBO in the blend resulted in a comparable improvement of the oxidative stability as 0.02 % BHA.
In the same direction Shiv K *et al. (*1983) reported that the oxidative stability of blends of palm olein and soybean oil was increased during a nine week storage period at ambient temperature compared to each individual oil.

TABLE 1.
FATTY ACID COMPOSITION OF SUNFLOWER OIL (SKO), SCLEROCARYA BIRREA OIL (SCO) AND MELON BUG OIL (IN WEIGHT %)

Fatty acids (%)	SKO	SCO	MBO	Part SCO in SKO (%)				Part MBO in SKO (%)			
				10	20	30	40	10	20	30	40
16:0	5.7	14.2	30.9	6.5	7.0	8.1	8.9	8.1	10.7	13.0	15.4
18:0	3.8	8.8	3.5	4.3	4.7	5.3	5.8	3.8	3.8	3.8	3.8
18:1	41.3	68.0	47.1	43.7	44.8	48.6	51.0	41.8	42.4	42.8	43.9
18:2	46.3	5.9	3.9	42.7	39.8	35.0	31.2	42.5	38.3	34.6	30.1

SKO: sunflower kernel oil, SCO: Sclerocarya oil, MBO: melon bug oil

TABLE 2.

OXIDATIVE STABILITY [h] (RANCIMAT 120 °C) OF SUNFLOWER OIL BLENDED WITH DIFFERENT AMOUNTS OF SCLEROCARYA BIRREA OIL (SCO) AND MELON BUG OIL (MBO).

The oil	IP in hours	% of IP increased
SKO (control) SCO MBO	1.9 43 38	
BHA (200ppm)	2.3	21%
SCO/SKO 1:9	2.8	47%
SCO/SKO 2:8	3.1	63%
SCO/SKO 3:7	3.7	95%
SCO/SKO 4:6	4.7	147%
MBO/SKO 1:9	2.0	5%
MBO/SKO 2:8	2.4	26%
MBO/SKO 3:7	2.8	47%
MBO/SKO 4:6	3.2	68%

SKO: sunflower kernel oil, SCO: Sclerocarya oil, MBO: melon bug oil

FIGURE 1.

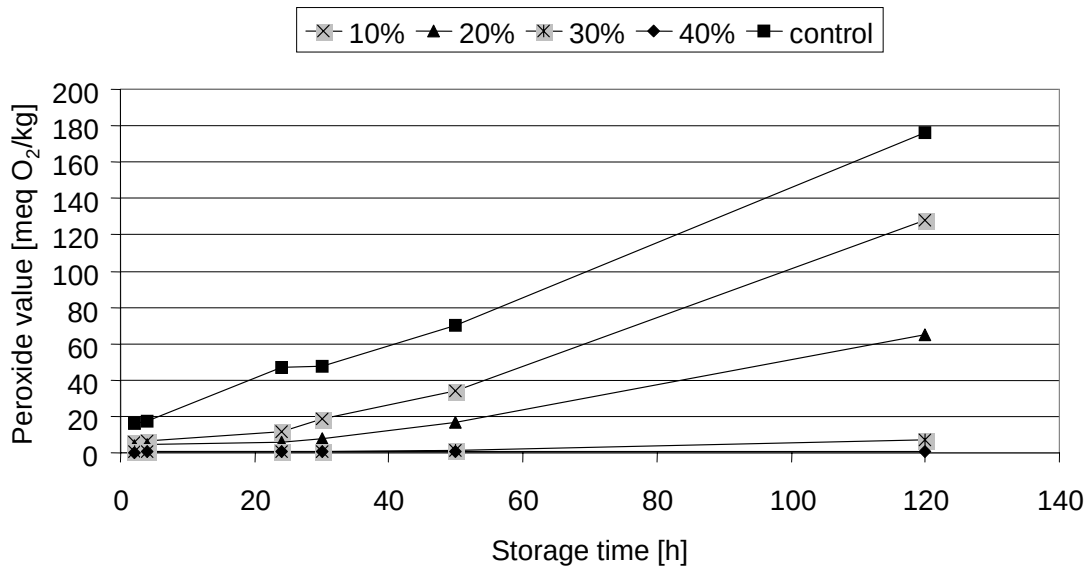
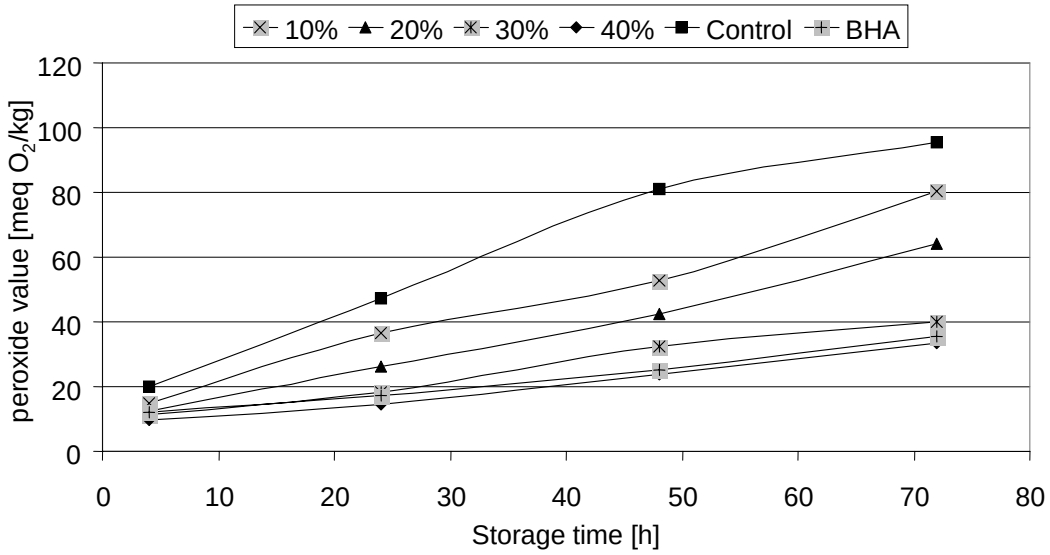


FIGURE 2.



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