The Effects of Extraction Methods on Sesame Oil Stability

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ABSTRACT: The oxidative stability of sesame oil, as measured by the Rancimat test, was shown to be dependent on extraction methods and seed pre-treatment. Oils extracted from whole seeds were more stable than those extracted from dehulled seeds by the same method. Extraction of the same seeds with polar solvents and effective seed crushing yielded more-stable oils (16.7–21.3 Rancimat hours) compared with extraction with nonpolar solvents and coarsely crushed or pressed seeds (4.5–6.4 Rancimat hours). Heptane–isopropanol (3:1, vol/vol) provided slightly more stable oils than *n*-hexane by the same method. Results are discussed in relation to some of the major anti- and prooxidants present in the oils.
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KEY WORDS: Antioxidants, dehulled seeds, extraction method, prooxidant metals, sesame oil, *Sesamum indicum*, stability, whole seeds.

Edible sesame seed (*Sesamum indicum* Linn.) has a high content (*ca.* 50%) of an oil with superior oxidative stability compared with several other vegetable oils, both at storage temperatures (1,2) and during frying (3). Despite these merits, sesame oil is only a minor edible oil, due to low yield and difficulties in mechanized harvesting (4). Its use is restricted to the areas of production and as a "gourmet oil" in industrialized countries (5).

The fatty acids of sesame oil are palmitic (7–12%), stearic (3.5–6%), oleic (35–50%), and linoleic (35–50%) (6). Crude sesame oils extracted from natural seeds contain *ca.* 45–68 mg% total tocopherols, which are mainly (95–99.5%) γ-tocopherol (7). The oil is characterized by the presence of a number of compounds from the furofuran family, mainly sesamin and sesamolin (7). Sesamol (8,9) and four other antioxidants are also present in sesame seeds in small amounts (10). Sesamol can be liberated from sesamolin during acid clay bleaching (8), hydrogenation (11), and frying (12). The antioxidant factors, responsible for the stability of sesame oil, seem to be highly affected by the different treatments, and each differently processed oil seems to have a characteristic combination of antioxidant factors, which has not yet been specifically defined.

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Because sesame seeds are mainly products of developing countries, full technological optimization of seed processing and/or oil extraction has not yet been achieved. Sesame oil is normally obtained from unroasted seeds from which oil is extracted by simple mechanical pressing of the seeds or by pressing followed by solvent extraction. Oxidative stability, an important characteristic of the oil, is expected to be influenced by the extraction method as well as seed treatment prior to extraction (13–15). This paper is a preliminary study on the effects of some processing conditions, namely extraction of differently processed seeds (whole/dehulled), with different extraction methods and solvents, on the stability of this oil. The Rancimat equipment was used in this investigation as the first indication of stability.

MATERIALS AND METHODS

Commercial whole and dehulled sesame seeds were from El Salvador and were supplied by Bodén and Lindberg, Ltd. (Täby, Sweden). The seeds contained *ca.* 3% moisture prior to extraction. Oils were extracted in the laboratory with *n*-hexane and HIP (heptane–isopropanol, 3:1, vol/vol) in a Soxhlet apparatus for 6 h, by vigorous shaking of the seeds in stainless-steel tubes with four steel balls and 30 mL for 1 h as described by Appelqvist (16) or after homogenization for 10 min in Ultra-Turrax equipment (Janke & Kunkel GmbH, Breisgau, Germany). Solvent-extracted oils were dried over anhydrous Na_2SO_4 and filtered, and the solvents were evaporated *in vacuo* at *ca.* 30°C. Solvent extraction yielded *ca.* 52% oil from the whole seeds and *ca.* 55% oil from the dehulled seeds. The seeds were cold-pressed for 2–3 min in a 12-ton capacity Carver laboratory press, according to manufacturer's instructions (Freds S. Carver Inc., Wabash, IN). The oils were in contact with the stainless-steel pressing equipment for 5–6 min. Pressing of the whole seeds yielded about one-third of the oil obtained by solvent extraction.

The oils were analyzed for tocopherols and lignans (sesamol, sesamin, and sesamolin) as previously described (7). Trace metals (iron and copper) were analyzed with a Varian Atomic Absorption Spectrometer (AAS 10; Palo Alto, CA), essentially according to IUPAC (17). The chlorophyll content of the oils was determined spectrophotometrically (18).

Oxidative stability indices (OSI) were determined for duplicate samples (2.5 g) with a 679 Rancimat instrument (Metrohm Ltd., Herisau, Switzerland) at 110°C (19). Glassware was routinely cleaned as previously described (20). Oil samples were weighed out in the reaction vessels, and those were placed into the heating block for 10 min to preheat the sample before air was supplied at a flow rate of *ca.* 10 L/h.

RESULTS AND DISCUSSION

Table 1 shows the effects of seed dehulling and of different extraction methods and solvents on oil stability and on the concentrations of some pro- and antioxidant constituents of sesame oils obtained from the same seeds. Oils extracted from whole seeds were more stable than those extracted from dehulled seeds with the same solvent and method. Differences in composition (levels of γ-tocopherol, sesamol, sesamolin, and trace metals) seem insufficient to explain differences in stability. Soxhlet-extracted oils showed higher concentrations of copper ions in the dehulled seeds. Large differences in stability between oils from dehulled and whole seeds were observed for oils extracted with HIP in the steel tubes. This suggests the presence of some unknown antioxidant factors or synergists in sesame hulls, which need effective grinding to release them. Peanut oils from dehulled beans were also less stable than those extracted from skinned beans (13). Recently, antioxidant factors were isolated from peanut (21) and rice hulls (22).

Solvent extraction of oils from whole sesame seeds was attempted by three extraction methods and two solvents for each extraction method. Oils extracted in the Soxhlet were of comparable stability to oils extracted by pressing. Extraction methods involving effective seed crushing and cold solvents (steel tubes and homogenizer) yielded considerably more-stable sesame oils than methods for coarsely crushed seeds and heat (pressing and Soxhlet). This can be related to the high extractability of prooxidants by hot extraction and/or to the release of more antioxidants due to effective seed crushing. Extraction with HIP (3:1, vol/vol) provided more-stable oils than extraction with *n*-hexane under the same conditions. The contribution of the extraction method to the stability was, however, greater than the contribution of the extraction solvent.

Table 1 also shows the relation between OSI of the differently extracted oils and the concentration of some important constituents of sesame oil. All seven oils showed only a trace amount of sesamol (<0.01%) and approximately the same levels of chlorophyll (*ca.* 3 ppb). Sesamolin, a precursor to sesamol, was slightly better extracted under hot conditions. The very unstable oils, obtained by pressing (*ca.* 30°C) or by reflux in the Soxhlet, were especially characterized by higher levels of copper ions compared with oils that were extracted under cold conditions in the stainless-steel tubes or the homogenizer. Apart from the pressed oil, no major variations in the contents of iron in relation to method were observed. The levels of iron detected in this study may not be effective factors in oil stability because the highly stable oils extracted in the steel tubes contained higher levels of this metal compared with the less-stable ones extracted in the homogenizer. Copper ions are known to be effective prooxidants in lipid oxidation (23). The low stability of the oils obtained by pressing and by Soxhlet extraction can thus be related, at least in part, to the high extractability of the prooxidant copper ions. On the other hand, the variations in the levels of the known antioxidants (γ-tocopherol and sesamol) and the possible antioxidants (sesamolin and sesamin) in the oils extracted by different methods are not significant and cannot explain the differences in the stabilities of the oils. Because sesamolin, which may liberate sesamol at high temperatures (11), was better extracted under Soxhlet conditions, it seems that the prooxidant effects of the trace metal ions were stronger than the antioxidant effects of the possibly released sesamol.

The fact that oils extracted by HIP had higher stability than those extracted with hexane by the same method, in spite of the higher tocopherol levels and lower ferric and copper concentrations in the latter oils, is worth noting. The more polar solvent, HIP, is better in extracting certain lipid components, e.g., glyco- and phospholipids, which were reported to act as

TABLE 1
Effects of Seed Dehulling and Extraction Methods and Solvents on Oil Stability and the Concentrations of Some Pro- and Antioxidants

Extraction method	Stability (h)	Level in oil (mg/kg oil)				
		γ-Tocopherol	Sesamolin	Sesamin	Iron	Copper
Pressed oil (whole seeds)	6.1	615	3010	3102	1.1	0.06
Soxhlet extraction (6 h)						
n-Hexane (whole seeds)	4.5	506	3540	3310	0.3	1.4
HIP[a] (whole seeds)	6.4	423	3800	3600	0.6	2.1
HIP (dehulled seeds)	5.6	395	3470	3220	0.6	3.2
Steel-tube extraction (1 h)						
n-hexane (whole seeds)	20.2	505	3300	2960	0.4	0.02
HIP (whole seeds)	21.3	419	3300	3480	0.7	0.02
HIP (dehulled seeds)	12.3	399	3290	2980	0.6	0.01
Homogenizer extraction (10 min)						
n-Hexane (whole seeds)	16.7	472	3010	3010	0.1	0.01
HIP (whole seeds)	18.6	460	3010	3100	0.4	0.02

[a]HIP = heptane–isopropanol (3:1, vol/vol).

synergists to antioxidants or as prooxidants, depending on the system (24). Extractability of the phospholipids is known to be dependent on the extraction method in accordance with the results obtained in this study. Extraction of flaked seeds, where extensive rupturing of cell walls occurs, is expected to yield more phosphatides than simple grinding in the mortar before Soxhlet extraction. Phospholipids also are better extracted by solvents than by pressing and have better extractability under hot than under cold extraction conditions. Phospholipids are suggested as antioxidants or synergists, because many crude oils are more stable than refined oils (25). Phospholipids have no antioxidant activity per se but are potent synergists, most probably due to trace-metal chelation (26). Sesame oil was mentioned early to contain small amounts (0.03–0.13%) of phosphatides (27). The composition of these phosphatides and their contribution to the stability of sesame oil have not yet been reported and warrant future investigation.

Kikugawa *et al.* (9) suggested the presence of some unknown antioxidants in sesame seeds and oil. Antioxidant plant phenols and phenolic acids also are expected to be present in seed hulls (21,22), and HIP is expected to be a better solvent in their extraction than hexane or pressing. Gutfinger (28) showed that olive oil extracted with chloroform–methanol was more stable than mechanically pressed oil and attributed the stability to the higher content of phenolic compounds in the solvent-extracted oil (321–574 ppm) compared with the pressed oil (50–159 ppm). Pokorny' *et al.* (29) claimed that the apparent antioxidative activity of isolated plant phospholipids may be due to contaminating phenolic compounds. Apart from the mention of trace amounts of ferulic acid in one sesame oil sample (12), there are no reports in the literature about the contents of phenolics in sesame seeds.

The results from this study suggest that sesame seeds need further studies to evaluate their antioxidant potential. Analysis of the seeds (hulls) for the content and composition of phospholipids and plant phenolics seems highly warranted.

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