Degumming and Bleaching of *Lesquerella fendleri* Seed Oil

Kenneth D. Carlson* and **Robert Kleiman**
USDA, ARS, NCAUR, NCR, Peoria, Illinois 61604

A lesquerella species (*Lesquerella fendleri*) being investigated as a domestic source of seed oil containing hydroxy fatty acids shows good agronomic properties and is being tested in semi-commercial production. *Lesquerella fendleri* seeds contain 25% oil, of which 55% is lesquerolic acid (14-hydroxy-*cis*-11-eicosenoic). Oils produced in pilot-plant quantities by screw press, prepress-solvent extraction and extrusion-solvent extraction processes have been refined in the laboratory by filtering, degumming and bleaching. Two American Oil Chemists' Society (AOCS) standard bleaching earths and two commercial earths were compared for effectiveness in bleaching these dark, yellow-red, crude lesquerella oils. Free fatty acids (1.3%), iodine value (111), peroxide value (<4 meq/kg), unsaponifiables (1.7%) and hydroxyl value (100) were not significantly affected by degumming and bleaching, but phosphorus levels of 8–85 ppm in the crude oils were reduced to 0.5–1.1 ppm in the degummed and bleached oils. Crude oils had Gardner colors of 14, which were reduced to Gardner 9–11 in the degummed and bleached oil, depending on bleach type and quantity used. AOCS colors in the range of 21–25R 68–71Y were obtained. By including charcoal in the bleaching step, a considerably lighter oil could be obtained (Gardner 7).

KEY WORDS: Bleaching, color, degumming, lesquerella oil.

Hydroxy fatty acids are used in many items of commerce, some of which have critical and strategic applications. The United States has been dependent on the world marketplace for its hydroxy fatty acids since domestic castor production was abandoned in 1971.

Lesquerella species contain hydroxy acid seed oils that are viewed as complementary to, and perhaps in some uses substitutes for, castor oil and its derivatives (1). Agronomic, breeding and chemical evaluations (2–6) suggest good potential for *Lesquerella fendleri*. The agronomic properties of this species are being tested in semi-commercial production with private-sector cooperation, including oil production and evaluation. Both laboratory and pilot-plant processing of the seed have been pursued to identify suitable conditions for commercial extraction of the oil. Also, rat-, chick- and beef-feeding studies are under way to evaluate the nutritional quality of defatted lesquerella meals.

Crude oils produced in our pilot-plant extraction studies (7) were dark due to abundant yellow and red pigments. These oils required refining to remove meal fines, gums and color before further evaluation and use. Therefore, both prepress-solvent extracted and extruded-solvent extracted oils have been filtered, degummed and bleached, and the results are reported in this paper.

EXPERIMENTAL PROCEDURES

Materials and methods. Crude oils from prepress, solvent extraction (designated hereon as prepress-solvent) of lesquerella seed consisted of 16.0 kg press oil [4-in (10.2 cm) mechanical press; French Oil Mill Machinery Co., Piqua, OH] and 21.4 kg solvent oil (4-stage miscella batch extraction of press cake; French deep-bed modular extractor). Crude oils from extrusion direct solvent extraction (designated hereon as extrusion-solvent) of flaked lesquerella seed (7) consisted of 11.3 kg oil batch solvent extracted (tank percolation) and 27.4 kg solvent oil continuously solvent extracted (Crown Model 2 extractor; Crown Iron Works Co., Minneapolis, MN).

Four bleaching earths were tested: Filtrol Nevergreen (Engelhard Corp., Edison, NJ), American Oil Chemists' Society (AOCS) Activated Bleaching Earth, AOCS Natural Bleaching Earth (AOCS, Champaign, IL), and Tonsil L-80 (L.A. Salomon Inc., Port Washington, NY). Darco G60 activated charcoal (ICI U.S. Inc, Wilmington, DE) was used in a few experiments to test additional color removal from lesquerella oil.

Oil analyses followed Official AOCS Methods (8): Ca 5a-40 [free fatty acids (FFA)]; Ca 12-55 [phosphorus (P)]; Cd 1-25 [iodine value (IV)]; Cd 8-53 [peroxide value (PV)]; Ca 6b-53 (unsaponifiable); Cd 13-60 (hydroxyl).

Degumming. The crude oils were first filtered through celite and No. 1 Whatman filter paper (Maidstone, England) to remove sludge (meal fines and gums) and then were refined. After a number of trials, the following degumming procedure was chosen. Crude oil was shaken vigorously in 2-L separatory funnels with 8% (w/w) saturated NaCl solution. Water alone (8% w/w) generally gave more difficult emulsions than the salt solution and therefore was not used further after initial trials. Depending upon the tenacity of emulsions formed, gums were separated by allowing the oil/salt solution mixtures to stand for different periods of time followed by centrifuging ($2500 \times g$). Where emulsions persisted, they were separated from the main fractions (oil and salt solution) and accumulated for further separation at a later time. Heating of both the oil and salt solution (70°C) prior to mixing gave only marginally better separation of emulsions and gums and therefore was not routinely practiced. Degummed oils were stored under nitrogen at 1°C in 1-gal (3.78 L) glass containers.

Bleaching. Initially, degummed oil was dried for 1.5 h in a rotary evaporator at 60°C and −98 kPa (29-in vacuum, water aspirator) prior to bleaching. However, experiments with both dried and undried oils showed that there were no differences in bleached color observed between dried and undried oils.

Bleaching parameters (bleaching earth type and amount, temperature and time) were initially evaluated by placing 43 g of degummed oil in 100-mL round-bottom flasks, adding the required amount (2.5, 5, 7.5 or 10%) of one of four bleaching earths mentioned above, and rotating the mixtures at 170 rpm on a rotary evaporator under vacuum (−98 kPa) at the desired temperature (60 or 80°C) for the desired time (1 to 3 h). These experiments identified 5% Filtrol Nevergreen bleaching earth, 80°C and 2 h as adequate for the maximum reduction observed in oil color. Thus, the bulk degummed oils were bleached by combining oil (900 g) with 5% Nevergreen bleaching

*To whom correspondence should be addressed at USDA, ARS, NCAUR, 1815 North University Street, Peoria, IL 61604.

earth (45 g) in 2-L round-bottom flasks and rotating the mixtures at 170 rpm and 80°C under −98 kPa vacuum for 2 h, after which the mixtures were centrifuged at 2500 × *g* until clear, bright bleached oils were obtained (*ca.* 2 h). Bleached oils were stored at 1°C under nitrogen in glass bottles.

Color measurements. Both crude and refined (degummed and bleached) lesquerella oils were compared for color in four color measuring devices: two provided Gardner colors (Gardner Tube Color Standards, Gardner Laboratory, Inc., Washington, D.C.; and Lovibond 3-Field Comparator, The Tintometer Co., Williamsburg, VA; 50 mm depth), one measured AOCS red and yellow colors (Tintometer Model AF 710; The Tintometer Co., AOCS Method Cc 13b-45) and the fourth measured Lovibond (red, yellow, blue and neutral) colors photoelectronically (Lovibond Colourscan instrument, The Tintometer Co.). On the dark, crude oils, AOCS and Lovibond colors could only be determined on 1-in (2.54 cm) oil depths, but colors of refined oils were read at the preferred 5 1/4-in (13.3 cm) depth.

Refined lesquerella oils sometimes remained slightly turbid or hazy after warming to room temperature from refrigeration, and it was necessary to warm them to 50–60°C to obtain a clear, bright oil for color determination. To determine any effect of temperature on color (clarification, density changes), color determinations (red, yellow, blue, neutral) were replicated with the Colourscan instrument on a refined lesquerella oil and on a commercial food oil (Mazola oil, local supermarket) at both room temperature and at 55°C.

RESULTS AND DISCUSSION

Crude lesquerella oils were available from pilot-plant trials of two oil extraction processes, prepress-solvent extraction and extrusion-solvent extraction. Quantities of the various press and solvent oils from these processes are listed in Table 1. All were dark yellow-red oils with Gardner colors of 14–15. A total of *ca.* 76 kg of oil was refined (degummed and bleached) in lots of *ca.* 0.9 kg each. Recovery of oil from degumming operations averaged 85.9% [standard deviation (SD) = 8.0, relative standard deviation (RSD) = 9.3%] for the prepress-solvent extraction oils, compared with 91.3% (SD = 3.4, RSD = 3.7%) for the extruded-solvent extraction oils. The lower recovery, and greater variability in that recovery, for the former oils undoubtedly resulted from their greater diversity (press *vs.* solvent, *etc.*) compared with the more uniform oils of the second group, which were all obtained by direct solvent extraction of extruded collets. Significant portions of oil entrapped in the emulsions that formed during degumming and mechanical losses account for the lower than desired recoveries.

Significant autodegumming occurred during initial storage of the crude prepressed solvent-extracted oils, whereas little similar action was observed during initial storage of the crude extrusion-solvent oils. This was apparent both from the amount of "sludge" ("foots") removed during initial filtration and from the amount of gums actually precipitated during degumming operations.

Four available bleaching earths were tested for bleaching power. Table 2 shows the results at three levels of bleach (2.5, 5, 7.5%) and for the combination of bleach (5%) and activated charcoal (3%). Although the bleach/charcoal combination produced the lightest oil (Gardner 7), charcoal treatments were not pursued further due to difficulties associated with the practical use of charcoal. Both Filtrol Nevergreen and AOCS Activated Bleaching Earth (acid activated clays) provided the best color improvement of the four earths (see 5% level, Table 2). With AOCS activated earth, 2.5% was definitely inferior to 5%, and 7.5% was not significantly better than the 5% level. Although Nevergreen and AOCS activated earths gave comparable color reductions, the former was easier to remove, thus giving brighter oils after centrifugation. Therefore, 5% Nevergreen earth at 80°C and −99 kPa vacuum for 2 h was chosen for the bulk bleaching runs. These conditions gave refined oils with golden-yellow colors (Gardner 10–11, Table 1). Bleaching recoveries for the two types of oils, prepress-solvent (90.0%, SD = 4.7%, RSD = 5.2%) and extrusion-solvent (87.1%, SD = 3.2%, RSD = 3.7%), were

TABLE 1

Colors and Refining Recoveries of Lesquerella Oil from Two Extraction Processes

Oil type	Crude oil (g)	Gardner color	Refined oil (g[a])	Gardner color	Recovery (%)
Prepress-solvent extraction					
Press oil, 1[b]	4214	14	2970	10	70.5
Press oil, 2[c]	11856	14	8686	10	73.3
Solvent oil, 3[d]	12495	15+	9078	11+	72.7
Solvent oil, 4[e]	8899	14	6064	[f]	68.1
Subtotal/average	37464		26798		71.5
Extrusion-solvent extraction					
Solvent oil, 5[g]	11343	14	9076	11+	80.0
Solvent oil, 6[h]	14378	14	11637	11+	80.9
Solvent oil, 7[h]	12951	14	10598	11+	81.8
Subtotal/average	38672		31311		81.0

[a]Filtered, degummed and bleached.
[b]Includes oil from full-press test run.
[c]Prepress conditions.
[d]Extracted from press cake.
[e]Direct solvent extraction of pelleted flakes.
[f]Brown tinge made color match difficult.
[g]Batch direct solvent extraction of multiple-pass extruded collets.
[h]Continuous direct solvent extraction of single-pass extruded collets.

TABLE 2

Gardner Color of Lesquerella Oil in Preliminary Bleaching Tests[a]

	% Bleaching earth			
Bleaching earth	2.5	5.0	7.0	5 + 3 C[b]
AOCS Natural Bleaching Earth	—	13	—	—
AOCS Activated Bleaching Earth	11+	10	9+	7
Harshaw/Filtrol Nevergreen	—	10	—	7
Salomon Tonsil L-80	—	13	—	—

[a]Oil (43 g) and bleaching earth were mixed for 2 h at 80°C and −99kPa vacuum.
[b]Darco G60 activated charcoal.

TABLE 3

Comparison of American Oil Chemists' Society Colors of Lesquerella Solvent Oils from Tintometer and Lovibond Colourscan Instruments[a]

	Tintometer oil depth		Colourscan oil depth	
	1-in[b]	5 1/4-in	1-in[b]	5 1/4-in
Crude oil 5[c]	15R 70 + Y	—	16R 69Y	—
Crude oil 6[d]	17R 70 + Y	—	18R 71Y	—
Crude oil 7[d]	16R 70 + Y	—	32R 82Y	—
Refined oil 5[c]	—	21R 70 + Y	—	35R 68Y
Refined oil 6[d]	—	20R 70 + Y	—	24R 69Y
Refined oil 7[d]	—	20R 70 + Y	—	22R 68Y

[a]Flaked seed extruded and then direct solvent extracted. Refined oils were degummed and bleached (Table 2). R = red, Y = yellow.
[b]1-in = 2.54 cm; crude oils were too dark to use 5 1/4-in (13.3 cm) tubes.
[c]Batch solvent extraction of multiple-pass extruded collets.
[d]Continuous direct solvent extraction of single-pass extruded collets.

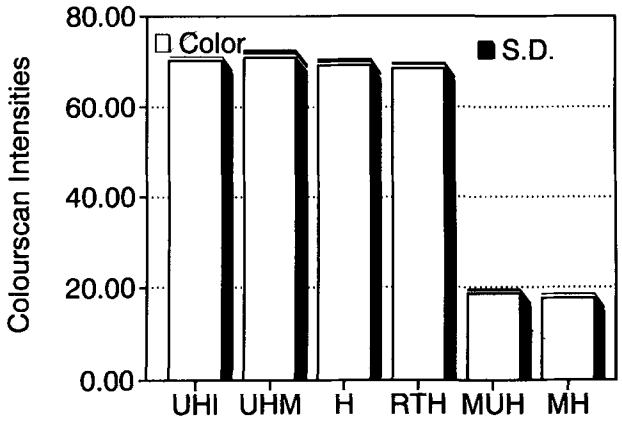

FIG. 1. Yellow color mean and SD of heated (55°C) and unheated (22°C) refined oils. UHI = unheated lesquerella oil, one sample read five times, instrument replication test; UHM = unheated lesquerella oil, mean of two sets of five replicates each read once; H = heated lesquerella oil, mean of five replicates; RTH = H samples, read at room temperature 72 h after heating; MUH = unheated Mazola oil, mean of five replicates; MH = heated Mazola oil, mean of five replicates.

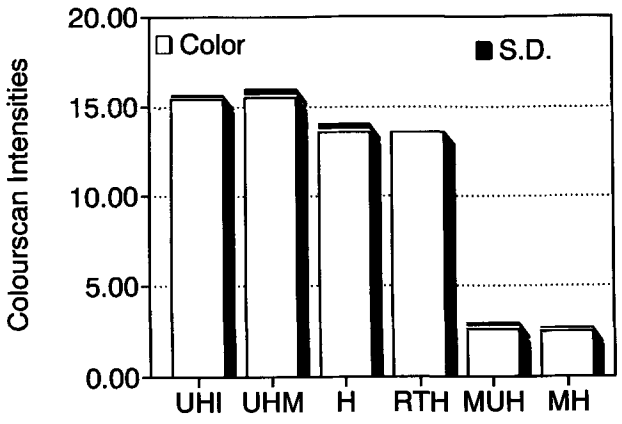

FIG. 2. Red color mean and SD of heated (55°C) and unheated (22°C) refined oils. See Figure 1 for sample and treatment identification.

similar in quantity and in variability, in contrast to the degumming data where differences between types of oils were more apparent. As shown in Table 1, overall recoveries were significantly better (81 *vs.* 72%) for the refined extrusion processed oils than for the prepress-solvent processed oils. Since more than 40 degumming and 40 bleaching runs were carried out on each type of oil, a significant portion of the oil losses were mechanical. Generally, we observed that solvent-extracted oils were more difficult to refine than press oils, and solvent-extracted oils from press cake were more difficult to refine than solvent-extracted oils from flakes and collets.

Table 3 compares AOCS colors of crude and refined lesquerella oils measured with the Tintometer and Lovibond Colourscan instruments. The crude oils were too dark to measure at an oil depth >1-in. Refined oils could be measured at the preferred 5 1/4-in depth. The Tintometer (visual color matching) gave essentially no differences in color between the several crude or between the several refined oils. The Colourscan instrument (electronic color measurement), however, recorded greater red values for crude oil 7 and refined oil 5 compared to the rest. We noted that lesquerella oil slowly crystallized when stored at 1°C for extended time periods. When warmed to room temperature, the oils sometimes retained a slight turbidity, which possibly was caused by waxes or other crystalline materials that dissolved or melted when the oil was warmed to 50–60°C. Colors in Table 3 were read on oils that had not been warmed above room temperature. To test the Colourscan's reproducibility with our lesquerella oils and the effect of oil temperature on color, the following experiments were conducted: The same aliquot of a refined lesquerella oil was read five times at room temperature (instrument replication, unheated, UHI); five aliquots of this unheated oil were read once each, a second set of five aliquots of this unheated oil were read once, and the combined data mean was computed (unheated, UHM); five aliquots of this oil were each heated to 55°C and each was read once (heated replicates, H); the heated replicates stood at room temperature for 72 h and were then read again at room temperature (heated/room temperature, RTH); five aliquots of a commercial food oil (Mazola) were read at both room temperature (Mazola unheated, MUH) and at 55°C (Mazola heated, MH). Figures 1-3 show the results of these experiments. Figure 1 shows that sample and instrument replication as well as temperature had

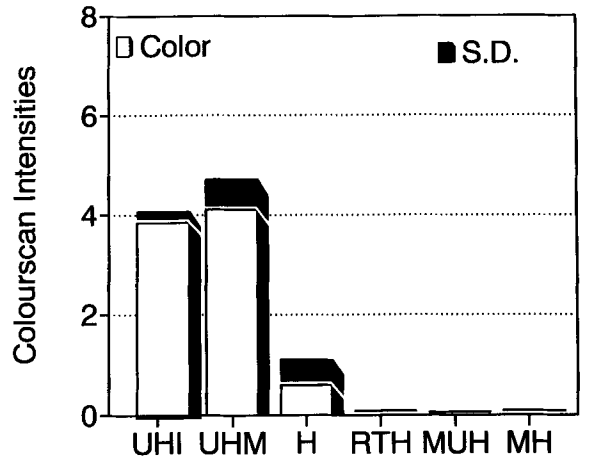

FIG. 3. Blue color mean and SD of heated (55°C) and unheated (22°C) refined oils. See Figure 1 for sample and treatment identification.

TABLE 4

Chemical Analysis of Crude and Refined Lesquerella Oils[a]

Oil type	FFA (%)	P (ppm)	IV (cg/g)	PV (meq/kg)	Unsap (%)	Hydroxyl (mg/g)
Crude oil 5[b]	1.3	8.3	111	3.6	1.7	100
Refined oil 5[b]	1.4	0.6	112	10.9	1.6	99
Crude oil 6[c]	1.2	18.0	111	3.4	1.7	98
Refined oil 6[c]	1.2	0.9	112	3.0	1.5	100
Crude oil 7[c]	1.3	85.0	110	2.3	1.6	101
Refined oil 7[c]	1.3	1.1	112	1.8	1.6	101

[a]Flaked seed extruded and then direct solvent extracted. Refined oils were degummed and bleached (Table 2). Abbreviations: FFA, free fatty acids; P, phosphorus; IV, iodine value; PV, peroxide value; Unsap, unsaponifiable.
[b]Batch direct solvent extraction of multiple-pass extruded collets.
[c]Continuous direct solvent extraction of single-pass extruded collets.

only small effects on yellow color in both lesquerella and Mazola oils. The figure also illustrates the much greater (3.5-fold) color intensity of our degummed and bleached lesquerella oil compared to the familiar consumer product.

Figure 2 shows that the red color in lesquerella oil was slightly more sensitive than the yellow color to replication and instrument errors (*cf.* UHI, UHM), but was particularly sensitive to temperature—the red intensity decreased at the higher temperature (H *vs.* UHM). If the slight turbidity in lesquerella oil, after warming to room temperature from refrigeration, was due to microcrystals, then these should have melted when the oil was heated to 55°C. This phenomenon may be responsible for the 9% decrease in red color intensity at 55°C. On this basis, no change in red color (H *vs.* RTH) was expected after the oil had stood at room temperature for 72 h, because the oil remained clear and bright (no recrystallization). The red color associated with the clear, light yellow Mazola oil (*ca.* 1/8 the red intensity of lesquerella) should not have been affected by temperature, as was observed (MUH *vs.* MH).

Figure 3 shows that the small blue color component of lesquerella oil was also sensitive to sampling and instrument errors and to temperature. The H lesquerella oil had only about 1/4 the blue intensity of the UHM room temperature oil, and this small component was not detected after 72 h in RTH. The MUH and MH oil had no blue color component.

Table 4 shows analyses obtained on crude and refined lesquerella oils prepared by extrusion-solvent extraction processes. As expected, most of these analyses were not affected by degumming and bleaching steps, so FFA contents, IV and hydroxyl values and levels of unsaponifiable material were similar for crude and refined oils. These values are also independent of the mode of solvent extraction (batch or continuous). PVs depend more on oil abuse (thermal and oxidative) during recovery, storage and later refining and were more variable. P contents are especially sensitive to processing conditions, such as mode of extraction, seed preparation and cooking. Degumming/bleaching effectively reduced P levels to 1 ppm or less in the refined lesquerella oils.

In general, we believe that colors of the refined lesquerella oils produced in this work are satisfactory for many uses of the oil or its derivatives. However, there will be other uses where lighter color will be important, and more effective bleaching processes will be necessary. Reducing the red component would be a useful goal. In a preliminary alkali refining experiment, we obtained abundant and difficult emulsions. However, the alkali-refined oil had less color (Gardner 10) than the crude oil (Gardner 14), and showed significant improvement in final bleached color (Gardner 7 with 2.5% Nevergreen; Gardner 6 with 5% Nevergreen). A combined alkali refining/degumming step will probably work well with low-FFA crude oils. Therefore, further alkali refining experiments are warranted, especially where low FFA levels are also desired in the refined oil. As more uses are explored and products are developed, the importance of oil color in specific applications will likely become more apparent.

ACKNOWLEDGMENT

The authors acknowledge the excellent technical assistance of Mark E. Klokkenga.

REFERENCES

1. Roetheli, J.C., K.D. Carlson, R. Kleiman, A.E. Thompson, L.K. Glaser, M.G. Blase and J. Goodell, *An Assessment of Lesquerella as a Source of Hydroxy Fatty Acids for Industrial Products*, Office of Agricultural Materials, Cooperative State Research Service, U.S. Department of Agriculture, Washington, D.C., 1991.
2. Thompson, A.E., in *Arid Lands: Today and Tomorrow*, edited by E.E. Whitehead, C.F. Hutchinson, B.N. Timmerman and R.G. Varady, Westview Press, Boulder, 1988, pp. 1311–1320.
3. Thompson, A.E., D.A. Dierig and E.R. Johnson, *J. Arid Environ. 16*:331 (1989).
4. Chaudhry, A., R. Kleiman and K.D. Carlson, *J. Am. Oil Chem. Soc. 67*:863 (1990).
5. Carlson, K.D., A. Chaudhry and M.O. Bagby, *Ibid. 67*:438 (1990).
6. Carlson, K.D., A. Chaudhry, R.E. Peterson and M.O. Bagby, *Ibid. 67*:495 (1990).
7. Carlson, K.D., R. Kleiman, L.R. Watkins and W.H. Johnson, Jr., in *New Industrial Crops and Products*, edited by H.H. Naqvi, L. Estilai and I.P. Ting, Office of Arid Lands Studies, College of Agriculture, University of Arizona, Tucson, 1992, pp. 169–175.
8. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 3rd edn., edited by R.E. Walker, American Oil Chemists' Society, Champaign, 1983.

[Received January 8, 1993; accepted April 2, 1993]