Extraction and Refining of Oil from Amaranth Seed

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Oil was extracted with hexane on a pilot plant scale from seeds of *Amaranthus cruentus* after the seeds were subjected to an efficient abrasive milling. Optimum conditions were then determined for refining and bleaching this oil. The yellow oil obtained is similar in appearance and composition to corn oil, but comparison with previously published analyses reveals a considerable variation in the content of the principal fatty acids, palmitic, oleic and linoleic, although the squalene content (5–8%) was in the expected range.

There is renewed interest (1–3) in the grain amaranths that will produce good yields of cereal-like seeds under arid conditions and in poor soils where conventional cereal crops do not grow well (4). The composition of seeds from several species of *Amaranthus* has been reported in detail (5), and the protein, starch and oil are of good quality for food and feed use (5,6).

The oil in amaranth seed is similar in composition to that in corn or cottonseed oil, containing principally triglycerides of linoleic, oleic and palmitic acids with very little linolenic acid (1,5,7,8). Other lipid components that have been reported are phospholipids and glycolipids (7), sterols (8) and squalene (5). Since the oil content of the seed is low, commonly 6–9%, it usually would not be extracted from the seed, but there may be occasions when it would be advantageous to use the oil and oil-free meal separately. This paper reports the pilot scale extraction of oil from the seed of *Amaranthus cruentus* and a study of the refining and bleaching of this oil.

MATERIALS AND METHODS

Amaranth seed. Seed of *Amaranthus cruentus,* which was obtained from the Guadalupe Natural Products Co., Austin, Texas, contained 9.8% moisture, 14.9% crude protein (N × 6.25), 6.2% oil, 2.2% ash and 0.49% crude fiber. These seeds are light colored and about 1.2 mm in diameter.

Extraction. Seeds were first extracted on a small scale (30 g) in a Soxhlet extractor after grinding in different mills to determine the most efficient pre-treatment. Mills tested were a Wiley mill, a hammer mill with a 0.84 mm screen, a single disk attrition mill (CE-Bauer, style 148-8, 8114X plates) and an abrasion mill (Morehouse Model 530), 0.36 mm gap. In the pilot plant, 67.3 kg of seed, ground in the Morehouse abrasion mill as above, was extracted at 69 C with 168 l of hexane for 22 hr in a Butt or Soxhlet-type extractor. Distillation of hexane from the extract, finishing under vacuum, yielded 4.03 kg (5.99% yield, as is) of dark, turbid oil with a strong odor. The extracted seed meal, 61.5 kg when desolventized, contained 8.4% moisture, 18.9% crude protein, 0.99% oil, 2.8% ash and 27% crude fiber.

Degumming and dewaxing. The crude oil was stirred with 1% water for 15 min at 60 C, then allowed to stand overnight at room temperature. The clear amber-brown oil was separated from gums by centrifugation at 1250 × G. This oil was dewaxed by cooling to 4–6 C for 4–10 days under nitrogen, then centrifuging at 19,600 × G, 4 C.

Refining. Alkali refining was done essentially according to AOCS Official Method Ca 9a-52 (9) with some modification to a reduced scale (10). NaOH solutions of

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TABLE 1

Yield of Oil from Milled Amaranth Seed

Milling[a]	Yield of oil, % mfb[b]
None	0.22
Wiley mill: 20 mesh screen	6.35
40 mesh screen	6.81
Hammer mill, 0.84 mm screen	6.43
Attrition, single disk	6.84
Abrasion mill	7.01

[a]See descriptions in Materials and Methods.
[b]Extraction of 30 g seed in Soxhlet with hexane.

TABLE 2

Effect of NaOH Concentration on Refined Oil

NaOH conc °Be'[a]	% Oil recovery	Absorbance 478 nm[b]	534 nm[b]	607 nm[c]	670 nm[c]
0	Unrefined	>1	0.230	0.102	0.342
12	89.5	0.350	0.060	0.023	0.103
14	89.4	0.369	0.060	0.023	0.090
16	89.3	0.355	0.060	0.019	0.082
18	89.4	0.367	0.069	0.022	0.079
20	88.7	0.375	0.073	0.025	0.081

[a]0.40% excess NaOH added.
[b]Shoulder.
[c]Maximum.

TABLE 3

Effect of Excess NaOH on Refined Oil

% Excess NaOH[a]	% Oil recovery	Absorbance 478 nm[b]	534 nm[b]	607 nm[c]	670 nm[c]
0.10	93.0	0.445	0.098	0.042	0.185
0.20	92.0	0.398	0.079	0.033	0.123
0.40	89.3	0.355	0.060	0.019	0.082
0.60	87.7	0.341	0.055	0.018	0.075

[a]16° Be' NaOH.
[b,c]See Table 2.

TABLE 4

Effect of Temperature on Bleaching[a]

Bleaching temp (°C)	FFA (%)	Peroxide value (meq/1000 g)	Absorbance 410 nm	478 nm	534 nm	670 nm
90	0.022	3.51	0.350	0.105	0.022	0.001
100	0.028	2.16	0.375	0.115	0.032	0.005
110	0.031	0.93	0.422	0.130	0.035	0.003
120	0.029	0.91	0.430	0.123	0.048	0.002

[a]15 min under N_2 with 2% Filtrol-4.

TABLE 5

Effect of Bleaching Clay Type on Properties of Bleached Oil

Filtrol bleaching clay[a]	FFA (%)	Peroxide value (meq/1000 g)	Absorbance 410 nm	478 nm	534 nm	670 nm
4	0.031	0.93	0.422	0.130	0.035	0.003
4[b]	0.028	0.46	0.387	0.117	0.032	0.008
105	0.030	0.45	0.400	0.131	0.074	0.004
105 FAC	0.024	0.34	0.370	0.128	0.089	0.003
105 FAC[b]	0.038	0.58	0.346	0.112	0.041	0.008
160	0.050	0.61	0.355	0.102	0.049	0.012
Nevergreen	0.023	0.37	0.390	0.135	0.090	0.009

[a]2% of oil, 15 min at 110 C under N_2. Filtrol clays from Harshaw-Filtrol Partnership.
[b]Also treated with 0.2% activated C (Norit A).

12° Be′ (8.0%) to 20° Be′ (14.4%) were added to the oil in amounts sufficient to neutralize the free fatty acid content of the oil plus a 0.1 to 0.6% excess (w/w, dry basis) of NaOH. The alkali was added to 150 g oil at 22 C in a stainless steel beaker with rapid stirring which was continued for 15 min. The beaker was moved to a 65 C water bath and the emulsion stirred slowly for 30 min at 65 C. The oil was cooled to 22 C for 1 to 4 hr and separated from the aqueous soap phase by centrifuging at 20,000 × G, 10 C.

Bleaching. Refined oil (100 g) was bleached by heating under nitrogen with various acid-activated bleaching clays. The temperature was varied from 90 to 120 C and the amount of clay from 2 to 6%. In some cases 0.2% of activated carbon (Norit-A) was added. After addition of bleaching clay, the oil was heated for 15 min, then cooled to about 75 C, mixed with 1% filter aid (Celite 545) and filtered through Whatman No. 5 filter paper. Bleaching clays tested (Filtrols-4, 105, 105 FAC, 160 and Nevergreen) were obtained from the Harshaw-Filtrol Partnership and were those designed for bleaching edible oils (11).

Color measurement and analyses of oil. Because a Lovibond Tintometer was not available in this laboratory, oil color was measured in a spectrophotometer between 350 and 750 nm using the neat oil in a cuvette with a 1 cm path length. This method had served as a useful substitute for use of the Lovibond color scale in a study of the refining of rice bran oil (10). Absorbance at 525–550 nm is closely related to Lovibond red, and the absorbance maxima at about 607 and 670 nm are characteristic of chlorophyll.

AOCS official methods (9) were used for the following analyses: No. Ca 5a-40 for free fatty acids (FFA), as oleic acid, and No. Cd 8-53 for peroxide value (PV). Both methods were modified for use of smaller samples and titration with a microburette.

Fatty acid composition was determined on methyl esters prepared from the oil using 14% methanolic BF_3 according to AOAC methods (12). The methyl esters were run isothermally at 185 C on a Hewlett-Packard 5890 gas chromatograph equipped with an OV 351 fused silica column (0.25 mm × 15 M) and a flame ionization detector. Injection and detection were at 220 C, and the fatty acid methyl esters were identified and quantified by comparison with a known standard methyl ester mixture.

Squalene in the oil was determined by HPLC at room temperature using Waters Associates equipment, a C18 column and a refractive index detector. The oil was dissolved in and eluted isocratically at 2 ml/min with 70:30 acetonitrile:THF. Identification and quantification were by comparison with standard solutions of squalene.

RESULTS AND DISCUSSION

There are no reported investigations of the processing of amaranth seed to facilitate extraction of the oil, but the milling characteristics and distribution of components in the seed have been described (13). Most of the oil was in

the seed coat-embryo fraction (25% of seed weight) which could be removed by abrasive milling (14). In the evaluation of different pre-treatments, highest yields of extracted oil were obtained after abrasive milling (Table 1), which was then used as the pre-treatment before pilot plant extraction of amaranth seed oil. Extraction probably could be done more efficiently if only the seed coat-embryo fraction, which can be separated by screening (14), was extracted.

Optimum refining conditions were determined after the dark, turbid crude oil was degummed (95% recovery) and dewaxed (96% recovery). The effect of alkali concentration was investigated, using a 0.4% excess of NaOH. In every case the free fatty acid (FFA) content, as oleic acid, was reduced from 2.37 to about 0.03%. The oil recovery and color (light absorbance) are indicated in Table 2. Oil color was reduced by refining to a medium yellow. The alkali concentration had only a slight effect on color but the color was lightest with use of 16° Be′ NaOH. Oil recovery was about 89.4%, becoming slightly less with use of 20° Be′ NaOH.

The effect of excess alkali, during refining with 16° Be′ NaOH, on oil recovery and color is indicated in Table 3. In every case the FFA was reduced to 0.03–0.04%. Both oil recovery and color intensity decreased as excess NaOH was increased from 0.1 to 0.6%. The bulk of the amaranth seed oil was refined with a 0.40% excess of 16° Be′ NaOH, since additional excess NaOH decreased the oil recovery but had a relatively minor effect on color reduction.

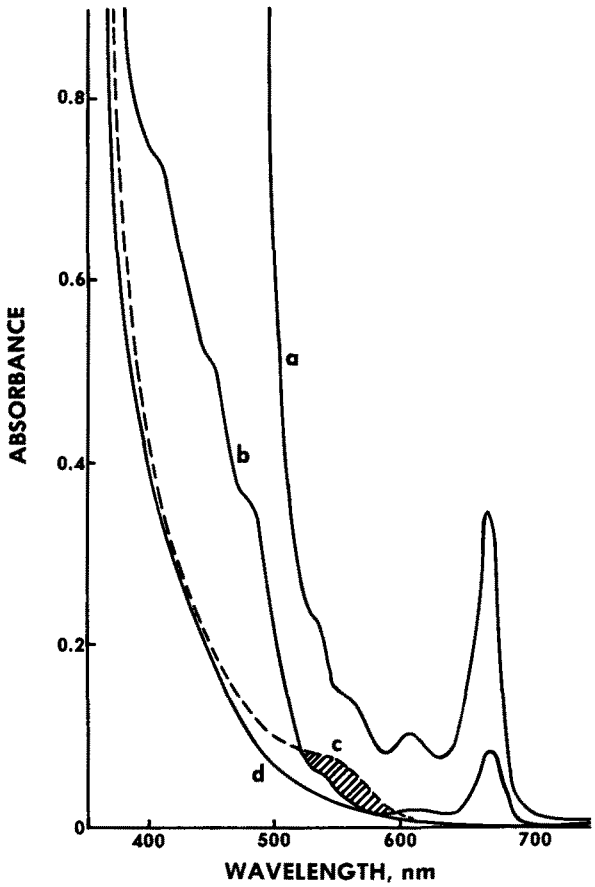

FIG. 1. Spectra of amaranth seed oils. a, degummed crude; b, refined; c, bleached with 2% Filtrol-105 FAC; d, bleached, then decolorized with 0.2% Norit-A.

TABLE 6

Fatty Acid Composition of Amaranth Seed Oil[a]

Fatty acid[b]	Crude oil	Bleached and decolorized oil
	wt %	wt %
16:0	13.4	13.9
18:0	2.74	2.61
18:1	20.4	19.8
18:2	62.1	62.0
18:3	1.06	1.09
20:0	0.66	0.61
Squalene[c]	6.96	8.01

[a]Average of 3 to 6 determinations.
[b]Percent of methyl esters.
[c]Percent of oil.

Suitable conditions for bleaching refined amaranth seed oil were then sought in a series of small scale tests at different temperatures and with varied amounts of a series of bleaching clays. The effect of temperatures from 90 to 120 C is indicated in Table 4. The color intensity increased with increasing temperature, but a temperature of 110 C was chosen as optimum because it was the lowest temperature at which peroxides were adequately eliminated.

Increasing the amount of clay (Filtrol-4) from 2 to 6% decreased the peroxide value from 0.93 to 0.41 meq/1000 g, decreased the red color (abs. at 534 nm) from 0.035 to 0.029 and the yellow color (abs. at 478) from 0.130 to 0.062, but also decreased the oil recovery from 95.6 to 94.3%. In actual practice, probably no more than 2% clay would be used because of the increased oil loss and cost of clay.

Five bleaching clays were evaluated at the 2% level at 110 C. In some cases the oil was also treated with activated carbon. Properties of the bleached oils are listed in Table 5. Light colored oils were obtained in all cases, with absorption at 670 nm due to chlorophyll eliminated and the peroxides adequately reduced. However, all the clays except Filtrol-4 yielded oils with a reddish tinge due to absorption at 534 nm. In fact, absorbance at 534 nm increased over that of the refined oil with use of all clays except Filtrols-4 and 160. Most of this reddish color could be removed by the use of 0.2% activated carbon in addition to the bleaching clay. The spectra of oils after different stages of processing are shown in Figure 1. The increased absorbance that causes a reddish tinge after bleaching with some clays is indicated by the shaded area.

The fatty acid composition and squalene content of the crude and bleached amaranth seed oils is indicated in Table 6. It is evident, by comparison with previously published analyses from this laboratory (5), that there is considerable variability in the composition of amaranth seed oil. In three samples of oil from different lots of *A. cruentus*, content of the principal fatty acids ranged as follows: 13–20% palmitic, 19–34% oleic, 37–62% linoleic. Composition of the fatty acids was not changed appreciably by degumming, refining and bleaching. All the

oils had a desirably low (@ 1%) content of linolenic acid, and the squalene content was high, as found previously (5). With its composition similar to corn and cottonseed oils, and its adaptability to conventional refining and bleaching procedures, amaranth seed oil could be a useful edible oil.

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REFERENCES

1. Saunders, R.M., and R. Becker, in *Advances in Cereal Science and Technology,* Vol. 6, edited by Y. Pomeranz, Am. Assoc. of Cereal Chemists, St. Paul, MN, 1984, pp. 357-396.
2. *Amaranth: Modern Prospects for an Ancient Crop,* National Academy of Sciences, Washington, DC, 1983.
3. Vietmeyer, N., *Ceres 15*(5):43 (1982).
4. Pal, M., and T.N. Khoshoo, in *Evolutionary Studies in World Crops,* edited by J. Hutchinson, Cambridge Univ. Press, New York, 1974, pp. 129-137.
5. Becker, R., E.L. Wheeler, K. Lorenz, A.E. Stafford, O.K. Grosjean, A.A. Betschart and R.M. Saunders, *J. Food Sci. 46:*1175 (1981).
6. Lorenz, K., *Staerke 33:*149 (1981).
7. Opute, F.I., *J. Exp. Botany 30:*601 (1979).
8. Fernando, T., and G. Bean, *J. Am. Oil Chem. Soc. 62:*89 (1985).
9. Official and Tentative Methods of the American Oil Chemists' Society, AOCS, Champaign, IL, 1973.
10. Sayre, R.N., D.K. Nayyar and R.M. Saunders, *J. Am. Oil Chem. Soc. 62:*1040 (1985).
11. Richardson, L.L., *Ibid. 55:*777 (1978).
12. AOAC, Official Methods of Analysis, 13th Ed., Association of Official Analytical Chemists, Washington, DC, 1980, pp. 211-222, 447.
13. Betschart, A.A., D.W. Irving, A.D. Shepherd and R.M. Saunders, *J. Food Sci. 46:*1181 (1981).
14. Becker, R., D.W. Irving and R.M. Saunders, *Food Sci. Technol.,* in press.

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