Color Problems in Oils from Experimental Safflower Varieties[1]

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Abstract

The dark color found in extracted oils from two new thin-hull safflower varieties is formed from a colorless precursor or precursors, which for convenience will be considered a single precursor. This precursor is extracted into the oil from the kernel portion of the seed with hot hexane. It condenses to a dark pigment, if heated for prolonged times in excess of 100C, and was found in varying amounts in hot extracted oils of pigmentless, brown-striped, and commercially grown Gila varieties. The color precursor can be removed from the oil by extraction with water or by alkali-refining. The dark pigment can be removed by treatment with dilute alkaline peroxide. Oil, free of pigment and pigment precursor, can be obtained if the press-cake or whole cracked seeds are extracted with hexane at room temperature.

Introduction

Breeding work on safflower is directed mainly toward obtaining higher oil content and meal protein. In the course of this work the University of Arizona, industry, and the USDA collaborated in the development and experimental planting of a thin-hull safflower variety, Arizona Brown Stripe. This seed contains about 47% oil, compared with a normal of about 36%, and contains more protein and less fiber in the remainder of the seed. Pilot-plant work was performed to determine whether normal oil processing methods would produce an edible quality of oil from Arizona Brown Stripe safflower seeds.

The conclusions were that the refining and bleaching procedures did not produce an oil comparable with domestic safflower oil. The experimental oil was darker in color, and a characteristic, straw-like odor carried through refining and bleaching. Deodorization apparently removed the odor, at least temporarily, but Brown Stripe oil remained much darker than commercial oil. This paper is concerned with the removal of this dark pigment and the prevention of its formation.

Experimental Procedures and Data

Materials

Two of the new thin-hull safflower varieties bred by Rubis at the University of Arizona (1) have been used in this study, Arizona Brown Stripe No. 12417 (ABS) and a pigmentless, striped variety (PS). A commercially grown Gila variety (G) was used for reference purposes.

Preparation of Oil Samples in General

The crude oils were obtained from the seeds by cracking the whole clean seeds in a disc mill, followed by either pressing and extraction of the press-cake or extraction only. The disc mill used was a Bauer Bros. Company Model 148, the press a heatable Charles F. Elms hydraulic press. For pressing, the cracked seeds were packed in 500-g or smaller portions in polypropylene twill, then pressed either cold (room temperature) or hot (press and seeds heated to 130C). Cold (room temperature) or hot (boiling) hexane was used for extractions. The solvent was added to the press-cake or to the cracked whole seeds in an amount sufficient to form a free-flowing slurry (one volume of seeds to two volumes of solvent), which was agitated in a Blendor for 2–3 min. Four to five such extractions, followed by filtration through fritted funnels, usually removed all the oil present in the seeds. The solvent was evaporated under vacuum at 60C and 18 mm Hg, and finally at 1 mm Hg. Duplicates of all samples (2 ml) were placed in open 2-ml screw-cap vials. One was used as an unheated control, and one was heated for 3 hr at 160C in a silicone oil bath. A 3-hr heating period at 160C has been chosen to measure color development after a relatively short time even though the maximum is not reached if the precursor is present at high concentrations.

Refining and Bleaching of Samples

Crude oils were refined by alkali-treatment, followed by clay bleaching. None of the samples were deodorized. Alkali-refining was performed by the addition of 2% of a 4N aqueous NaOH solution to the oil, followed by stirring at room temperature for 15 min and centrifugation. Special Filtrol Grade 4 was used for bleaching. The oil, to which 2% Filtrol was added, was stirred and heated to 115C for 15 min, after which it was centrifuged.

Spectroscopic Analysis of Samples

The spectroscopic properties of the oils were examined with a Cary Model 15 spectrophotometer at wavelengths between 300 and 800 mμ. Samples were measured directly (undiluted) in a quartz cell of 1-mm pathlength with hexane as a reference. Switch-over from tungsten to hydrogen lamp was at $\lambda = 400$ mμ. All samples were subjected to high-speed centrifugation ($35{,}000 \times g$ for 20 min) prior to measurement to obtain transparent oil samples suitable for qualitative and quantitative spectral analysis. Pigment (condensed color precursor) gave rise to a peakless absorption in the range of $\lambda = 500$ to 800 mμ with a strong increase toward shorter wavelengths (Fig. 1,

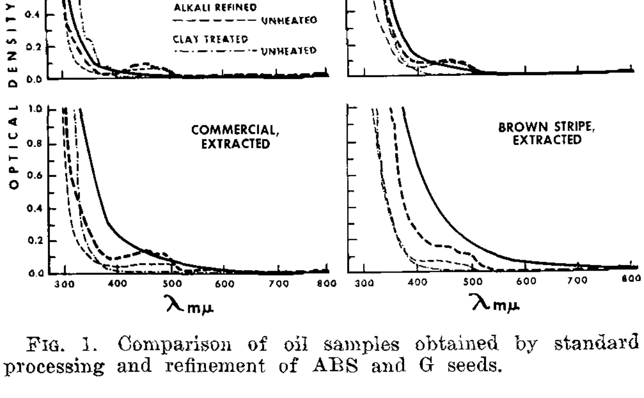

Fig. 1. Comparison of oil samples obtained by standard processing and refinement of ABS and G seeds.

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[1] Presented at the AOCS Meeting, Chicago, October 1967.
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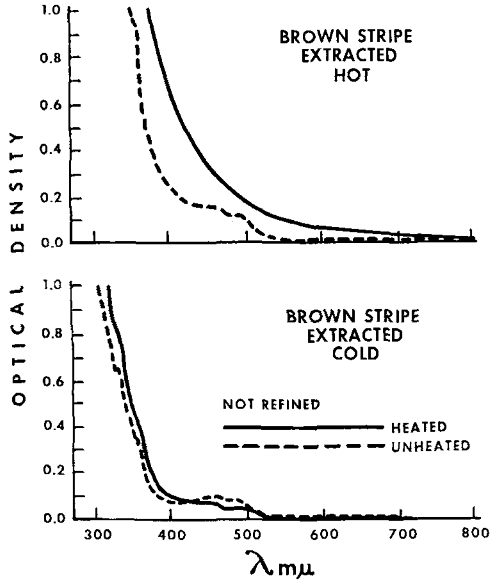

FIG. 2. Comparison of oil samples obtained from ABS seeds by extraction with cold and hot hexane.

3, and 5). Since the strong absorption below λ = 550 mμ overlapped with that of other safflower oil constitutents, pigment was measured at λ = 550 mμ, where all pigmentless oils were free of any absorption (Fig. 3 and 5). Visual appearance of pigment became apparent at optical densities greater than 0.05 and objectionable at twice that level. The color precursor did not show any detectable absorption between λ = 300 to 800 mμ and was therefore estimated as pigment, to which it was condensed by heating (3 hr/ 160C). Absorption maxima for a carotenoid substance found in all crude oil samples were 432, 458, and 482 mμ (Fig. 3 and 5). These peaks disappear when the oil is heated, indicating heat decomposition of the carotenoid substance. This heat-bleaching occurs in precursor-containing oils as well but is overshadowed by pigment formation.

Ordinary Processing of Seeds

ABS and G seeds (1,000 g) each were hot-pressed, followed by extraction with hot hexane. Total yield of crude oil was 45% for ABS seeds and 36% for G seeds. About 85% of the total oil yield was obtained by pressing and the remainder by extraction. The four crude oil samples were separately refined and spectrophotometrically measured (Fig. 1).

Extraction of Seeds with Cold Hexane

ABS seeds (1,000 g) were cracked and cold-pressed; the resulting press-cake was extracted with cold hexane. The yield of extracted oil after evaporation of the solvent was 17.4%. This oil was centrifuged and spectrophotometrically compared with the oil sample previously obtained from ABS seed by extraction with hot hexane after hot pressing (Fig. 2).

Oil Samples from Hulls and Kernels

ABS seeds were partially cracked and screened into three sizes of fractions. Hulls containing less than 1% kernel particles (200 g) were obtained from the fraction of the large particles by air separation. Kernels containing less than 1% hull particles (278 g) were obtained from the medium-size particle fraction after aspiration, followed by additional screening for size and final removal of a few heavier hull particles from the kernel fraction by hand.

The oil from the kernels was obtained by hot pressing and yielded 152 g = 90% of the total oil present in the kernels. Hot extraction of the kernel press-cake yielded another 16.7 g = 10%. Total oil obtained was 168.7 g = 61% of kernel weight. Hulls were not pressed but were extracted only with hot hexane; they gave 18 g of oil or 8% yield. The spectra of the centrifuged crude oils are shown in Fig. 3.

Removal of Pigment by Refining

An oil sample enriched in pigment was prepared for this purpose in the following manner. Arizona Brown Stripe kernels (935 g) were extracted three times with 1.0 liter of hexane at room temperature in a blendor and filtered. The extracts were combined, and the solvent was evaporated, leaving 521 g of oil = 56% yield. The residue was then further extracted with two portions of 900-ml boiling hexane to give another 54 g of oil = 6%. Total yield of oil was 515 g

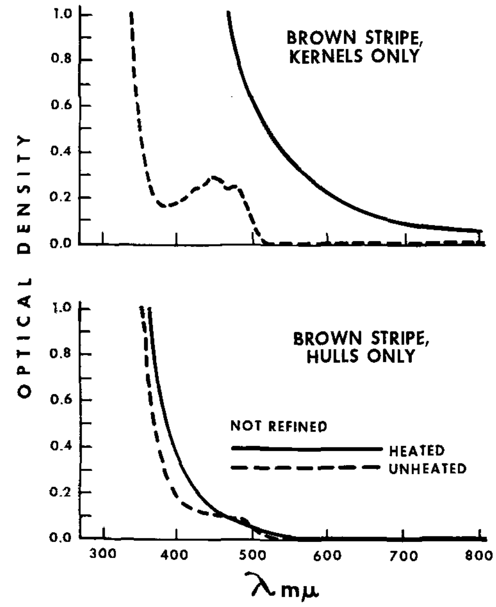

FIG. 3. Comparison of oils obtained from ABS seeds separated into kernels and hulls.

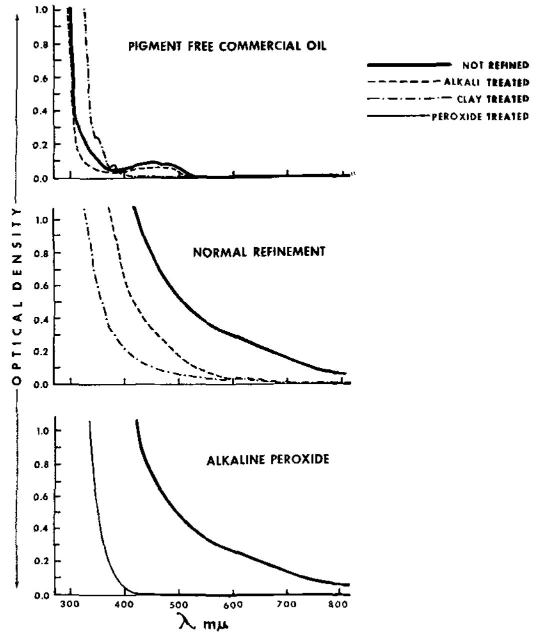

FIG. 4. Removal of pigment by normal and alkaline peroxide refinement from ABS oil.

or 62%. The oil obtained by extraction with hot hexane (54 g) contained almost all of the pigment precursor present in the 935 g of kernels and turned black when heated for 3 hr at 160C. One portion of the heated oil was subjected to alkali-refining and clay bleaching, which removed only part of the pigment (Fig. 4). A second portion was treated with 5% (v/v) of a mixture of 1 g KOH in 10 ml H_2O_2 (3%). The mixture was stirred at room temperature, and additional portions of 5% alkaline peroxide were added every 4 hr until all pigment was degraded (two to three additions were necessary). The resulting emulsion was centrifuged; the oil phase was washed with water (1:1/v:v) and again centrifuged. The resulting oil was almost colorless. Spectrophotometric measurements for all samples are shown in Fig. 4.

Removal of Precursor by Water-Extraction

Safflower oil (50 ml), rich in color precursor, was obtained from ABS kernels either after pressing by hot hexane extraction or, after cold hexane extraction, with hot hexane. The sample was partitioned with water (50 ml) and centrifuged. The supernatant oil phase was used as is and heated for spectrophotometric measurements. The aqueous phase was freeze-dried. The resulting residue was dissolved in 50 ml of commercial safflower oil, which was free of color precursor, and was used, heated and unheated, for spectral data collection (Fig. 5).

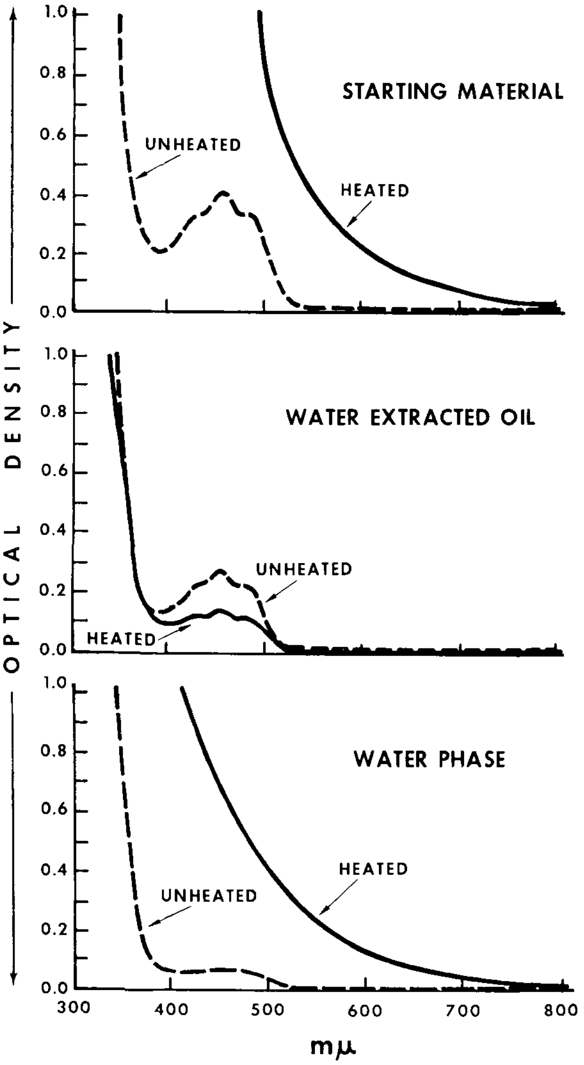

FIG. 5. Removal of pigment precursor by water-extraction (solid from water phase added to precursor-free oil).

TABLE I

Effect of Heating and Water Extraction on Safflower Oil Samples (O.D. × 1000 at $\lambda = 550$ mμ, Pathlength 1 mm)

Oil source	24C	100C	120C	140C	160C
	3 hr				
ABS, kernels only hot-extracted after pressing	33	43	86	1458	1558
Same oil as above, but water-extracted	6	6	6	5	6
G, whole seeds hot-pressed	2	1	1	1	0
G, whole seeds hot-extracted after pressing	6	9	16	175	262

Effect of Heating on Precursor

Four unrefined oil samples prepared earlier were used: a) ABS, kernels only, hot-extracted after pressing; b) same oil as before but water-extracted; c) G, hot-pressed; and d) G, hot-extracted after pressing. The samples were kept at different temperatures for given times, and their optical density was measured at $\lambda = 550$ mμ (Table I).

Discussion

This study establishes that the dark color found in extracted oil from two thin-hull safflower varieties is caused by a color precursor or precursors, which are converted to dark pigment if heated in excess of 100C for extended times (Table I). Color precursor was found in unrefined, extracted oils of all tested varieties, including the commercially used Gila seeds and the pigmentless thin-hull variety. It is concentrated in the kernel part of the seed (Fig. 3) and only removed by extraction with hot hexane. Cold or hot pressing and extraction with cold hexane do not remove the precursor from the seed. Commercial seed usually had the lowest and ABS the highest precursor content, but considerable variations were observed from one preparation to the other. The cause of these variations is presently under investigation. The color precursor can easily be removed by extraction with water. Once condensed to a dark pigment, it cannot sufficiently be removed by standard refining procedures if present at high concentrations. However, if dilute alkaline peroxide was used, all pigment from those samples could be removed in a one-step treatment without apparent changes in oil viscosity. This severe oxidation procedure is probably deleterious to the oil but is the only procedure found so far that removes color after it is formed.

Three laboratory methods of processing acceptable safflower oil from ABS and PS safflower have been successful in preventing color: a) pressing hot (up to 130C for 1 hr), followed by extraction with cold hexane; b) extraction of whole cracked seeds with cold hexane; c) pressing hot, followed by hot hexane extraction (temperatures not above 100C).

The first two methods yield crude oils which are free of pigment and precursor and will bleach upon heating. The third method yields pigment-free extracted oil containing the precursor. The precursor has to be removed with water or by alkali-refining before the oil can be heated without danger of color formation.

It has been observed that Method 2, where all the oil is obtained by extraction with cold hexane, yields the cleanest crude oils. In addition, it is the fastest method to obtain all the oil in only a few extractions in the laboratory. If industrial processing can be adapted to any of these three methods, the problem of dark color in oils from high-yield, thin-hull safflower varieties may be solved. Besides, plant breeders may attempt to breed new desirable safflower varieties which are free of color precursor. This study has established that it is not the melanin-pigment in the hull but the color precursor in the kernel which is directly linked to the dark color of the oil. A test will be devised shortly to screen existing collections and new breeds of safflower varieties for color precursor. Experiments are also under way to isolate and identify the precursor.

ACKNOWLEDGMENTS

Thanks are expressed to A. E. Goodban for helpful discussions and to Mrs. A. R. Gramps for technical assistance.

REFERENCE

1. Rubis, D. D., Proceedings of First Safflower Utilization Research Conference, in press.

[Received October 12, 1967]