A Quantitative Evaluation of a Color Problem in Safflower Oils

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Abstract

The dark color occasionally found in crude solvent-extracted oils from a new high-yield brown striped safflower variety originates from colorless precursors in the kernel and precursors in the hull. The precursors from the hull and the pigments formed upon heating from hull and kernel precursors are only partially removed by refining and bleaching if they are present in substantial amounts. The pigment precursors extracted from the kernels are completely removed by precipitation with water or refining. Although substantially more hull and kernel precursors are found in oil from the brown striped safflower variety, the oil can be produced in a spectrographic quality comparable to that of commercial oil if the crude extracted oil is not heated above 100 C, and if extracted and press oils are jointly refined.

Introduction

Earlier investigations of a color problem in extracted oil from a new high-yield safflower variety, Arizona Brown Stripe, showed that considerable amounts of dark pigment were formed upon heating from colorless precursors extracted from the kernel part of the seed (1). These precursors have now been identified as three common phosphatides (2). This paper is concerned with the role of precursors and pigments extracted from the hull and a more accurate quantitative and comparative analysis of the color problem in oils of the brown striped safflower variety in general.

Experimental Procedures and Data

Materials

The thin-hulled safflower variety, Arizona Brown Stripe, and commercial seed, preponderantly Gila, were used in this study.

Preparation of Oil Samples

Oils were obtained by pressing only at 120 C (P), by cold (room temperature) solvent extraction after pressing (EAPC), by hot (boiling point) solvent extraction after pressing (EAPH), by cold extraction only (EOC), by hot extraction only (EOH) by mixing nine parts of (P) oil with one part of (EAPC) oil, and by mixing nine parts of (P) oil with one part of (EAPH) oil. For each of the two varieties, 30 ml samples of crude oil were obtained from cracked whole seed by all of these methods, from pure kernels by P, EAPC, EAPH, EOC and EOH, and from pure hulls by EOC and EOH.

A 20 ml portion of each of the 28 crude samples was then refined with 4 N NaOH and one half of the refined sample bleached with clay. Each of the 84 samples (42 from each seed variety) was then examined spectroscopically before heating and after heating at 160 C for 3 hr. The more detailed preparation of the oil samples was performed as described earlier (1) except for the following variations: All oil samples prepared by pressing were pressed hot (120 C). The oils were bleached with 2% Filtrol 105 rather than with special Filtrol (115 C for 15 min). Spectroscopic examination was limited to measurement of absorption at 550 mμ for all samples of oil and 440 mμ for the bleached oils only. Light absorption was measured in microcells of 40 mm path length to obtain more meaningful values in the low absorption range of the refined samples. Samples with O.D. × 100 > 200 were measured in cells of 5 or 10 mm path length and values multiplied by factors of 8 or 4 correspondingly.

Results and Discussion

The data are summarized in Table I. Underlined values show the most important trends in oil color versus treatment.

The problem of dark color in the samples was analyzed at a wavelength of 550 mμ because at this wavelength there is no interference with absorption arising from other pigments commonly present in crude and alkali-refined oils (1). However, the bleached oil samples were measured at both 550 and 440 mμ since the pigments commonly present are completely removed at this stage of processing. Measurement at these two wavelengths allows one to convert values into the industrially used photometric index or to Gardner and Lovibond color values (AOCS Method Td2a-64 and Td1a-64T). Since Gardner and Lovibond values cannot be used to relate concentration and absorbance, we have reported color in units of absorbance × 100. Assuming that Beer's Law holds in the range we are studying, the figures in the Table are directly proportional to concentration of pigmented material.

In our earlier work we found that the major contribution to dark color which formed upon heating of crude extracted oils originated from color precursors extracted from the kernel while the contribution from the hull extracts was relatively small. The data available now (Table I) allow one to make a quantitative estimation of this contribution if one assumes the hull oil appears only in the extracted oil from safflower seeds. To calculate values for thin-hull oil No. 3 (extracted after pressing crude at 160 C), comparative absorbance values of oils from kernels (No. 10) and hulls (No. 14) have to be related to the kernel-hull weight ratio and oil yields. Brown striped seeds consist of about 80% kernel and 20% hull and the corresponding oil yields were 6% obtained by extraction of prepressed kernels and 8.6% obtained by extraction of hulls. The measured absorbance values for oils (No. 10 and 14) were 1172 and 414 respectively. A comparative figure representing the total amount of color formed from each source can then be computed by multiplication of these three values (80 × 6 × 1172 and 20 × 8.6 × 414). The result presented in percentages of total color formed is about 89% from the kernel and 11% from the hull pigments. An alternative method for calculation is to assume no interaction between hull oil and kernel oil, so that EAPH oil from whole seed has the same amount of color as a mixture of hull oil and kernel oil in the proper proportion. On this basis, for a unit amount of whole seed EAPH oil, if x is amount of kernel oil and y is amount of hull oil, $x + y = 1$.

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TABLE I
Spectroscopic Analysis of Oil Samples[a]

Condition	Temperature C	Wavelength mμ	Whole seeds							Kernels					Hul
			1 P[b]	2 EAPC	3 EAPH	4 EOC	5 EOH	6 1+2	7 1+3	8 P	9 EAPC	10 EAPH	11 EOC	12 EOH	13 EOC
Commercial seed															
Crude	RT[c]	550	1	7	12	1	3	2	4	0	5	15	0	1	13
	160	550	0[d]	189	533	2	32	12	13	0	87	651	2	30	9
Refined	RT	550	1	1	1	0	0	0	0	0	0	0	0	0	0
	160	550	0	0	0	0	0	0	0	0	0	0	0	0	0
Bleached	RT	550	2	3	5	4	2	2	2	2	3	3	3	3	4
	160	550	2	2	4	2	2	2	2	0	2	3	4	1	2
Bleached	RT	440	72	85	94	69	72	71	71	73	87	82	72	69	89
	160	440	58	65	71	58	59	52	61	56	64	60	62	56	48
Arizona brown stripe															
Crude	RT	550	5	39	57	4	6	6	9	1	8	12	2	4	22
	160	550	6	701	956	17	90	50	112	1	749	1172	6	41	78
Refined	RT	550	4	9	13	0	0	2	3	1	1	2	0	0	5
	160	550	2	9	13	0	0	2	4	0	1	0	0	0	10
Bleached	RT	550	2	5	6	4	2	2	2	0	3	3	2	2	5
	160	550	2	9	10	2	2	2	2	1	0	3	0	1	11
Bleached	RT	440	68	132	145	63	65	74	70	55	78	83	54	56	127
	160	440	61	127	142	57	61	66	65	47	55	65	47	46	161

[a] Absorbance, O.D. × 100.
[b] P, press oil; E, extracted oil; AP, after pressing; C, cold (RT); H, hot (69 C); EO, extracted only.
[c] Room temperature.
[d] Underlined values show the most important trends in oil color versus treatment.

Absorbtion values are x(1172) for kernel, y(414) for hull, and 1 (956) for whole seed. x(1172 + y(414) = 956. Solving for x and y, the volume of kernel oil is 0.72 and hull oil 0.28. The relative color contribution from kernel is 89%, from hull 11%. This is in good agreement with the calculation from actual relative volumes of oil, and indicates that pigment formation from hull and kernel oils occur independently.

These data confirm the importance of the kernel pigments relative to those of the hull. In addition, the kernel precursor content (phosphatide content) of crude-extracted brown stripe oil is much higher than that of commercial safflower oil (Table I, oil No. 3 from both varieties). We therefore believe that the very dark color of the extracted oil obtained during original industrial evaluation (3) of the brown-striped variety was mainly a result of heating kernel precursors. It is well known, however, that phosphatides can be removed from crude oil either by degumming or regular refining (4). Kernel pigments will form only if crude oils are heated to temperatures above 100 C prior to removal of phosphatides. Once formed in substantial amounts they can only partially be removed. In summary then, kernel pigments represent the greatest potential hazard as far as dark color-formation in safflower oils is concerned but they do not constitute any problem if their precursors are removed before the oils are heated.

The dark pigments extracted from the hull contribute only a minor part to total color but their precursors, in contrast to those of the kernel pigments, can only partially be removed by standard oil processing methods. An acceptable hull oil can therefore not be produced from the brown-stripe variety (Table I, oil No. 13). Pigments and precursors were also found in hull oils of commercial varieties but amounts varied from almost none for the variety reported in Table I (oil No. 13) to about half of that usually found in brown stripe hull oil for another commercial variety.

Hull pigments and precursors can be removed by standard oil processing methods from oils which contain substantial amounts if the corresponding oils are diluted with sufficient press oil before refining and bleaching. An example is shown in Table I for extracted brown stripe oil obtained after pressing from whole cracked seeds (oil No. 3); if processed as such the final clay-bleached oil still contains objectionable amounts of hull precursor and pigment. However, if this extracted oil is mixed with the press oil obtained before extraction of the press cake, the resulting bleached oil (Table I, oil No. 7) is acceptable in color before and after heating. (Arbitrarily we assumed that an absorption of <5 at 550 mμ represented an acceptable oil.) Likewise no color problem exists in bleached oils which are obtained from cracked seed by solvent extraction only (Table I, oil No. 5). The pigments and their precursors are completely removed by refining and bleaching.

We also investigated the effect of solvent-temperature on the extraction of pigment and precursor (Table I, oils No. 2, 3; 4, 5; 9, 10; 11,12) and found that the lower solvent-temperature substantially decreased extraction of pigments and precursors while oil yields dropped only slightly. Although these differences are reduced by pigment and precursor removal during refining and bleaching, the authors feel that extraction of whole seeds with solvent at room temperature (Table I, oil No. 4) presents by far the most advantageous method to separate oil from the seed compared to conventional methods actually being used. We see the following advantages in using this method: (a) all the oil present in the seed is obtained in one operation; (b) a very clean, crude and refined oil is obtained free of all the material soluble in hot hexane but not in cold solvent (2); and (c) convenience of all room temperature operation except for solvent removal.

The extracting solvent plays another important role as far as the spectrographic quality of the extracted oil is concerned. This has been discovered in the course of our work on the isolation and identification of the kernel-phosphatides (2). Very small percentages of contamination of the extracting solvent with dehydrating agents such as methanol, acetone, ethanol or others can easily change the extraction of pigment precursors from the kernel (phosphatides, gums) by factors of 10 or more (2). This phenomenon, we think, explains the large variations in pigment content found in heated extracted oils obtained from like sources.

Variations of this origin made it impossible to characterize oils of different safflower varieties by their

specific kernel pigment or phosphatide content as we attempted earlier (1). However, when hexane containing 3% methanol was used as extracting solvent we found that all safflower varieties tested had pigment and phosphatide contents which could be well reproduced. The varieties tested in this experiment included Gila, Arizona Brown Stripe, UC-1, a purple-striped and a pigmentless-striped variety. The values obtained did not show any striking qualitative and quantitative differences in pigment or phosphatide content while conventional extraction with hot hexane usually yields much higher values for the brown striped variety (Table I, oils No. 10).

We assume, at present, that these differences are based on slight varietal changes in the phosphatide-protein bond.

This detailed study has led to the conclusion that the color problem of extracted brown-striped oil can be solved if the oil is not excessively heated before bleaching and if extracted and pressed oils are jointly refined. All the oil of the high-yield brown-striped safflower variety can be reproducibly obtained by this method in a spectrographic quality similar to that of commercial oil (compare commercial oils No. 3 and 7 with brown-stripe oil No. 7 in Table I). We have also used this method in a pilot plant scale experiment, the results of which will be published later, and have obtained all the brown-stripe oil in an acceptable spectroquality. These results show that there is no reason remaining for the rejection of this new high oil thin-hulled variety because of inferior color quality of its oil.

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