Studies on the Pigments of Some Citrus, Prune and Cucurbit Seed Oils when Processed with or without Cottonseed Oil

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Pigments of citrus, prune and cucurbit fruit seed oils were studied spectrophotometrically. The citrus fruits used were: orange (O), mandarin (M), bitter orange (BO) and lemon (L). The prunes used were apricot (A), peach (P) and plum (PL); while melon (M), watermelon (WM) and Winter squash (S) were the cucurbits. Absorption spectra and Lovibond color were studied for crude, refined and bleached oils. Cottonseed oil (CSO) was mixed with some of the previous oils in the crude state, then refined and bleached. Absorption spectra of the crude fruit seed oils revealed carotenoid pigments at 400, 425, 455 and 480 nm, chlorophyll at 610 and 670 nm and unknown pigments at 525, 570 and 595 nm. Refining did not remove these pigments, whereas bleaching eliminated them completely. In oil mixtures of CSO + A, CSO + M and CSO + S, interference occurred between gossypol '360 nm' from CSO and the pigments of A, M and S seed oils. Refining the oil mixtures removed gossypol, but its effect on carotenoids, chlorophyll and unknown pigments was limited. Bleaching completely removed all these residual pigments. Lovibond color for all bleached oils was very low (0.2-2 yellow). The refined oils, except those containing Winter squash seed oil, were found to have an acceptable color (0.8-15 yellow). Results of the proposed process reveals the possibility of mixing crude edible oil with crude fruit seed oils, then processing the oil mixture by the conventional methods of refining and bleaching.

Total production of fruits in Egypt exceeds 3.7 million tons annually (1). Food industry companies produced more than 50,000 tons of preserved fruits (2), which results in a large quantity of wastes. Fruit seeds can be used as a good source of oil. Mean oil percentage was found to be 40-45% in citrus seeds (3), 42-45% in prune kernels (4,5) and 32-38% in cucurbit seeds (5). Both the chemical and physical characteristics of these oils were studied (3-5). From the nutritional point of view, some fruit oils are similar to some common edible oils in their chemical composition, e.g., citrus seed oils from orange, mandarin and lemon approximate the chemical composition of cottonseed and soybean oils (3). The citrus seed oils used were commercially produced in California (6). Apricot kernel oil has a good nutritive value (7) and has a composition similar to olive oil (8). Watermelon seed is used in India for edible purposes, and its oil is used in cooking (9). Winter squash oil is used in Australia as salad oil and has a composition approximating corn oil (10).

The aim of the present work is to investigate the pigments present in some groups of fruit seed oils, namely; citrus, prunes and cucurbits. The effect of conventional refining and bleaching techniques on these oils is also studied. Instead of processing these oils in small batches, which might not be economically sound, a proposed process of blending some of these crude oils with a crude edible oil, e.g., cottonseed oil, then carrying out conventional refining and bleaching is also investigated.

MATERIALS AND METHODS

The fruit seeds—citrus (Rutaceae): orange (*Citrus aurantium*), mandarin (*C. reticulata*), bitter orange (*C. aurantium*) and lemon (*C. limon*); prunes (Roseceae): apricot (*Prunus armeniaca*), peach (*P. persica*) and plum (*P. domestica*); and cucurbits (Cucurbitaceae): watermelon (*Citrullus lanatus*), melon (*Cucumis melo*) and Winter squash (*Cucurbita maxima*)—were collected in the different seasons of the year 1987. Seeds were washed from residues, dried in an oven at 60°C for 24 hr, and then dehulled and/or ground. The oils were extracted from the sieved fine particles of the seed kernels, with commercial hexane in a Soxhlet apparatus. After extraction, the solvent was evaporated at 50°C under vacuum in a rotary evaporator. Crude oils were kept in closed brown bottles in a refrigerator.

Cottonseed (*Gossypium barbadense*) Giza 75 was kindly supplied by the Ministry of Agriculture. The oil was extracted as mentioned before.

Crude fruit oils were refined and bleached individually or refined and bleached after their addition to crude cottonseed oil at a ratio of 1:1 by weight. For the refining process, 50 gm each of crude oils were placed in 200-mL beaker and heated to 60°C. The calculated amount of sodium hydroxide solution (18°Bé) was added according to the methods of the AOCS (11). The mixture was stirred for 30 min and centrifuged. The oil layer was then decanted and kept in a refrigerator.

Bleaching. Forty gm each of the refined oils was taken in a 200-mL beaker and heated in an oil bath at 110°C. Bleaching earth "Tonsil" was added at a ratio of 3% of the oil weight while stirring for 10 min. The mixture was centrifuged and the oil was decanted and kept in a refrigerator.

Spectrophotometric analysis of oils. In order to get reasonably representative absorption curves, oil samples have to be diluted with carbon tetrachloride at the following ratios by volume: 1:5 for crude fruit seed oils; 1:100 for crude cottonseed oil; 1:50 for the mixed crude oils (fruitseed oils + cottonseed oil); and 1:2 for all refined and bleached oils. Absorption spectra and analysis of oil samples were carried out in a Shimadzu UV-Visible Spectrophotometer, Model UV 240 Graphtcord (Shimadzu Corp., Tokyo, Japan). A wavelength range from 300-700 nm was used.

Color evaluation. Oil color was evaluated without dilution in a Lovibond tintometer as described in the AOCS methods (11). The color was expressed in yellow (Y), red (R) and blue (B) units.

RESULTS AND DISCUSSION

Figure 1A shows the absorption spectra of the crude

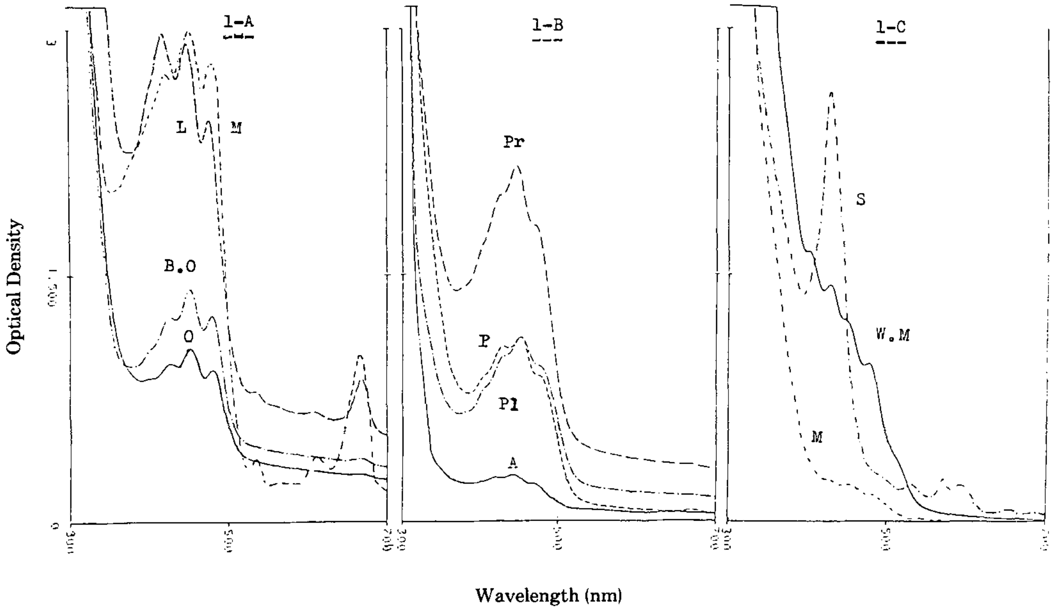

FIG. 1. Absorption spectra of crude citrus (A), prune (B) and cucurbit (C) seed oils. Symbols: O = orange; M = mandarin; BO = bitter orange, A = apricot; P = peach; PL = yellow plum; PR = red plum; WM = watermelon; M = melon; S = winter squash; and CSO = cottonseed oil.

citrus seed oils (orange, O; mandarin, M; bitter orange, BO; and lemon, L). Carotenoids and chlorophyll were found to be the major pigments. Carotenoids have absorption maxima at 400, 425, 455 and 480 nm. Chlorophyll appears at 610 and 670 nm in large amounts in M seed oil, and in relatively lower quantities in L seed oil. M and L seed oils have greenish yellow colors, whereas O and BO seed oils are yellow.

Figure 1B shows the absorption spectra of crude prune seed oils. In general, they have relatively less colors than citrus seed oils. Carotenoids are the only pigments that appeared in the spectra of this group. Comparing the four oils of this group, it can be seen that apricot kernel oil (A) possesses a superior bright yellow color, followed by peach (P) and yellow plum (PL) kernel oils, while red plum kernel oil (PR) has a reddish yellow color due to the increased amount of carotenoids.

Figure 1C illustrates the absorption spectra of cucurbit seed oils. Melon seed oil (M) has the lightest color, whereas Winter squash oil (S) is the darkest among all the fruit seed oils investigated, with a reddish brown color. The major band of carotenoid with a very high concentration appeared at 425 nm. It was reported that lutein represents 70% and β-carotene represents 12% of the carotenoids of squash seed oil (9). Besides its high content of lutein at 425 nm, S seed oil has unidentified pigments at 525, 570 and 595 nm and a small amount of chlorophylls at 610, 670 and 690 nm. Carotenoid pigments appear in M and WM at 400, 425, 455 and 480 nm.

Figure 2 gives the absorption spectra of the refined oils of citrus seeds (O, M, BO and L), prune kernels (A, P and PL) and cucurbit seeds (WM, M and S). Refining does not remove the carotenoids, chlorophyll or the unknown pigments. They still appear at their known positions at 400, 425, 455 and 480 nm for carotenoids, 610 and 670 nm for chlorophyll and 525, 570 and 595 nm for the unknown pigments.

Figure 3 shows the absorption spectra of the bleached oils of citrus, prune and cucurbit seeds. Bleaching completely removes all the bands of carotenoids, chlorophylls and unknown pigments. After bleaching, the oils acquire a very acceptable light color.

Figure 4 represents the absorption spectra of crude (C), refined (R) and bleached (B) cottonseed oil. Cottonseed oil is used as a control for the next proposed process. Crude cottonseed oil shows an absorption maximum at 360 nm, and this band belongs to gossypol. It is easily removed by refining. Refined cottonseed oil shows absorption bands of carotenoids at 400, 425, 455 and 480. Carotenoid pigments in the crude oil are masked by the high gossypol absorption and are eliminated by bleaching.

A proposed process includes mixing of crude oils before refining and bleaching in the following manner: (i) Crude cottonseed oil (CSO) + crude apricot kernel oil (A), 1:1 weight (curve CSO + A; Fig. 5A); (ii) CSO + crude mandarin seed oil (M), 1:1 by weight (curve CSO + M; Fig. 5B); and (iii) CSO + crude winter squash seed oil (S), 1:1 by weight (curve CSO + S; Fig. 5C).

Mandarin seed oil represents the citrus group, it contains the highest amount of carotenoids and chlorophyll among its group. Apricot kernel oil represents the lightest oil color among the prune group. Winter squash seed oil—with the darkest color and content of unknown pigments—represents the cucurbit group. Cottonseed oil, representing common edible oils, was selected as a control. It was mixed with the test oils because of its high gossypol content. The mixed oils

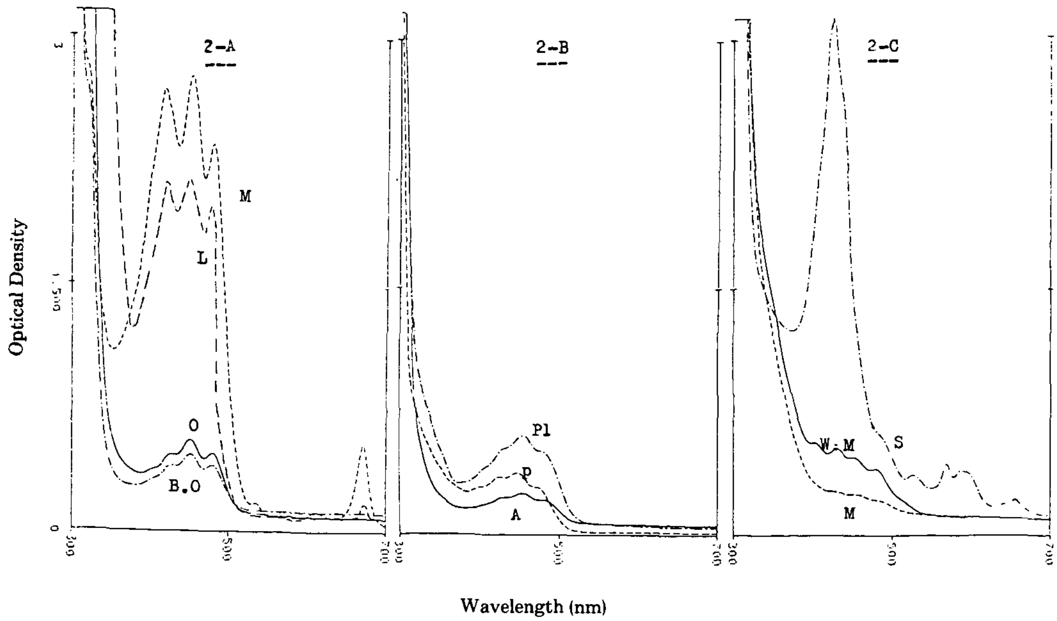

FIG. 2. Absorption spectra of refined citrus (A), prune (B) and cucurbit (C) seed oils. See Figure 1 for key to symbols.

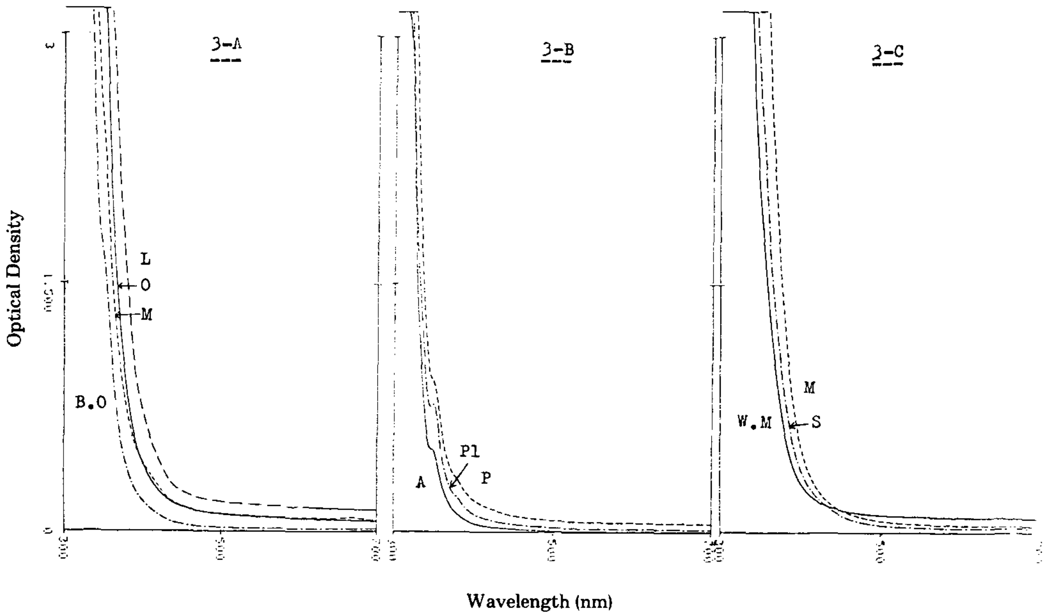

FIG. 3. Absorption spectra of bleached citrus (A), prune (B) and cucurbit (C) seed oils. See Figure 1 for key to symbols.

were then refined and bleached by the conventional methods.

From Figure 5A it can be seen that gossypol of crude cottonseed oil interferes with carotenoids of crude apricot kernel oil (curve CSO + A), crude mandarin seed oil (curve CSO + M) and crude winter squash seed oil (curve CSO + S). This interference results in the appearance of bands at 325, 378, 400, 425 and 480 nm. Maximum absorption of gossypol is shifted to 378 nm, and its shape becomes sinuous. Chlorophyll remains at its position at 670 nm.

Refining the oil mixtures (Fig. 5B) resulted in complete removal of gossypol, accompanied with the return of the carotenoid pigments to their original position at 425, 455 and 480 nm. Chlorophyll still appears at its position at 610 and 670 nm, and the unknown pigments were at 525, 570 and 590 nm.

Bleaching (Fig. 5C) ultimately removes all residual pigments from refined oil mixtures and results in acceptable bleached oil colors. Bleached CSO + S has a slightly higher color than the other two mixtures, CSO + A and CSO + M. Two carotenoid humps appear in bleached CSO + S at 425 and 480 nm, and one chlorophyll hump appears in bleached CSO + M at 670 nm.

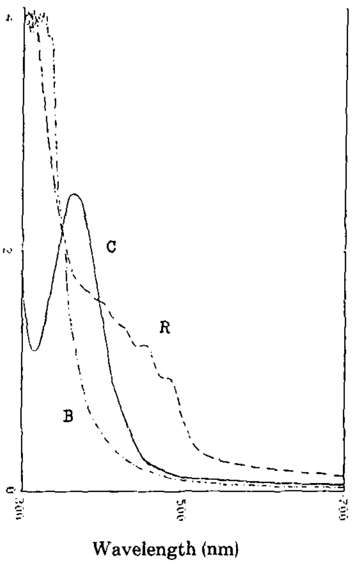

FIG. 4. Absorption spectra of crude (C), refined (R), and bleached (B) cottonseed oil.

The oil color on the Lovibond scale is illustrated in Table 1.

The color of the crude fruit seed oils of citrus, prunes and cucurbits ranges between very light for melon (0.9 Y), to deep yellow for plum red (17 Y), whereas winter squash seed oil was dark red in color (15 Y + 2 R + 0.3 B), and crude cottonseed oil—either alone or after mixing with one of the apricot, mandarin or winter squash seed oils—was a dark reddish brown (16 Y, 5-8 R and 6-7 B). The refining step was important in order to neutralize the acidity and to remove the impurities. The refined oils of the fruit seeds revealed a very slight difference with the crude oils, because the refining did not remove carotenoids or chlorophylls. The color of the refined oil of winter squash seed remained dark red at 15 Y + 1 R + 0.2 B. Refined cottonseed oil, or refined mixed cottonseed-apricot seed or cottonseed-mandarin seed oils were light in color (2 Y, 2 Y and 8 Y, respectively), because the gossypol in the mixtures was completely removed by refining. In spite of removing gossypol from refined cottonseed oil mixtures, the high content of carotenoids and chlorophylls still present retained a dark red color (at 9 Y + 2 R + 0.1 B). Owing to the light color of most of the refined seed oils or of the mixed cottonseed-fruit seed oils (0.8 Y to 15 Y), it is not necessary to bleach these oils when used as salad oil. However, it is important to bleach the refined winter squash seed oil if used

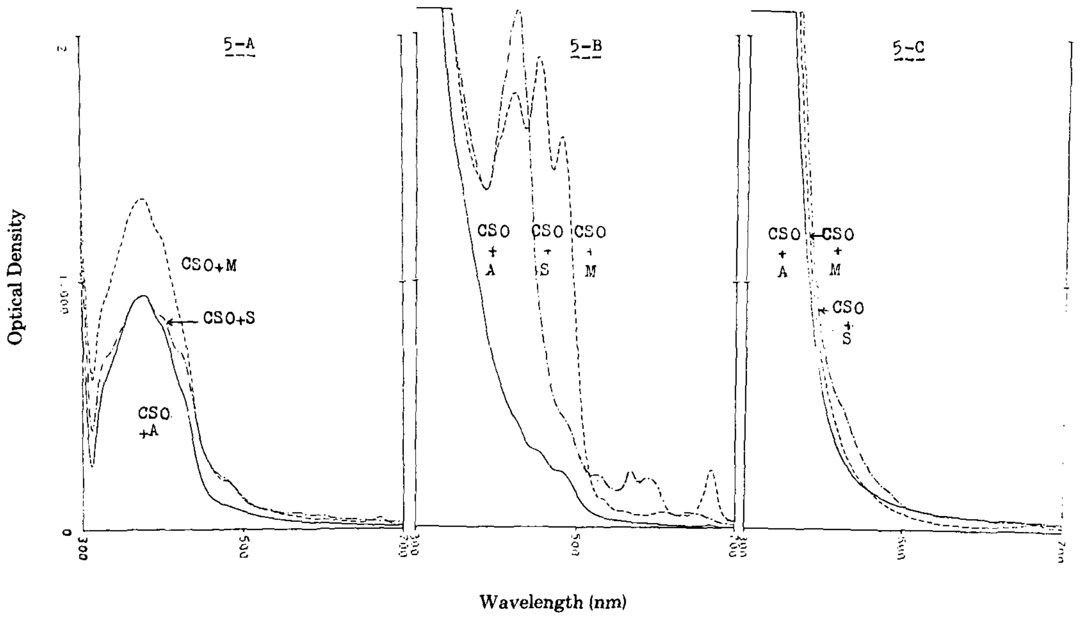

FIG. 5. Absorption spectra of mixed crude (A), refined (B) and bleached (C) oils. See Figure 1 for key to symbols.

TABLE 1

Oil Color in Lovibond Units

Oil	Crude	Refined	Bleached
Citrus			
Orange	10 Y[a]	9 Y	1 Y
Bitter orange	6 Y	6 Y	1 Y
Mandarin	14 Y	13 Y	1 Y
Lemon	12 Y	11 Y	1 Y
Prunes			
Apricot	3 Y	3 Y	0.8 Y
Peach	14 Y	12 Y	1 Y
Yellow plum	13 Y	12 Y	1 Y
Red plum	17 Y	15 Y	2 Y
Cucurbits			
Melon	0.9 Y	0.8 Y	0.2 Y
Water melon	5 Y	4 Y	1 Y
Winter squash	15 Y + 2 R[b] + 0.3 B	15 Y + 1 R + 0.2 B	2 Y
Cottonseed	16 Y + 6 R + 9 B[c]	2 Y	1 Y
Cottonseed + apricot	16 Y + 8 R + 6 B	2 Y	1 Y
Cottonseed + mandarin	16 Y + 5 R + 7 B	8 Y	1 Y
Cottonseed + w. squash	16 Y + 8 R + 6 B	9 Y + 2 R + 0.1 B	2 Y

[a]Y = yellow.
[b]R = red.
[c]B = blue.

alone or mixed with cottonseed oil. Bleaching for these oils resulted in a light yellow color. Lovibond color for the bleached oils ranged between 0.2 Y and 2 Y, and thus they can be used as frying oils.

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