Use of Ferric Chloride to Decolorize Cottonseed Oil

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Abstract

Cottonseed miscella was treated with $FeCl_3$ to form an iron-gossypol complex. The treated miscella was then extracted with alkaline water. The supernatant lipid filtered through bleaching clay produced an oil containing virtually no light-absorbing color bodies and a product that compared favorably, colorwise, with commercial oil.

Introduction

Almost one quarter of the cottonseed oil produced in the United States is sold at less than premium prices because of pigment content that cannot be readily removed. Furthermore, a large quantity of imported oil also fails to realize its full economic potential because of pigment content. These losses are of such a serious nature that better methods of oil cleaning are constantly sought. Several methods have been developed to remove pigments, particularly gossypol, from cottonseed oil. Reaction of the pigments with chemicals such as anthranilic acid (1), hydrogen peroxide (2), and sodium silicate (3), adsorption of pigments on chromatographic material (4,5), or a combination of the aforementioned methods has been suggested (6).

Most of these methods utilize either a potentially toxic or hazardous chemical, or are too limited in capacity for commercial usage. In this communication, we introduce a new method of pigment removal that is not toxic or hazardous and might be applicable to commercial production with a minimum of additional expense. The bases of this new method are that certain metallic ions, e.g., ferric ions (7), react with gossypol, the principle pigment in cottonseed miscella (8), and that the reaction product is removable.

Materials and Methods

Cottonseed miscella was obtained from flaked, glanded cottonseed (*Gossypium hirsutum,* L.) by extraction with either hexane-acetone-water azeotrope (HAW) (9), or hexane. An estimate of the gossypol content in the miscella was made from the absorbance at 360 mμ of the oil in spectrograde hexane using the absorptivity, 334 liters $gram^{-1}$ cm^{-1} (8).

Solvent was removed from the miscella in vacuo and the oil was dissolved in hexane to a solution of 10% oil (v/v). Ferric chloride dissolved in acetone was then added for a 1:1 molar ratio with gossypol. The amount of ferric chloride-acetone corresponded to 10% of the volume of oil-hexane. The addition caused dense formation of black, inky material. After a few hours, 1.5 vol of 0.1 N NaOH were added to form an underlay into which much of the black precipitate and pigmented material entered. The upper, nonaqueous phase was passed through a layer of neutral, activated bleaching clay (Bennett-Clark Co.) corresponding to approximately 1:1 (w/w) clay to oil. Solvent was removed in vacuo and absorbance of light by the oil was determined. Control samples of oil were treated as above except ferric chloride was absent from the acetone.

Spectrophotometric determinations were made with Beckman Model DU and Model DK-2 recording spectrophotometers. Appropriate dilutions of the material to be analyzed were made in spectrograde hexane. Contents of free fatty acids were determined by titration according to the official methods of the AOCS (10), except that the indicator Nile Blue was substituted for phenolphthalein to overcome the difficulty of observing red color changes in a reddish milieu.

Results and Discussion

Figures 1 and 2 show spectra of cottonseed oils, obtained by HAW or hexane extraction, before and after treatment of the oils. Absorbance occurring at 360 mμ (characteristic of gossypol) was virtually eliminated by the treatment with $FeCl_3$. Indeed, they were spectrophotometrically similar to commercial cottonseed oil (Fig. 2) even though they were not steam deodorized, a process which also removes some pigments.

Data in Table I, calculated from Figures 1 and 2 with corrections for dilutions, show the relative amounts of color due to pigments in the oils absorbing at 360 mμ. Oil from the HAW miscella contained over 1000-fold more color than commercial oil and over 40-fold more than oil from hexane miscella, yet was decolorized with the ferric chloride method to a level comparable to commercial oil. Oils from the HAW or hexane miscella were decolorized partially or completely, respectively, by the control procedure that had no ferric chloride present. Apparently, the addition of 0.1 vol of acetone followed by the alkaline wash and clay filter was sufficient to remove some pigment from oil. In the case of the oil extracted by hexane, which oil had a relatively low content of pigment, the amount removed comprised all of the pigment (Fig. 2). However, the presence of $FeCl_3$ resulted in additional pigment removal, yielding an oil that was almost 10-fold cleaner than oil prepared without ferric chloride (Fig. 1).

Although the detailed mechanism of oil decolorization with ferric chloride is uncertain, at least two

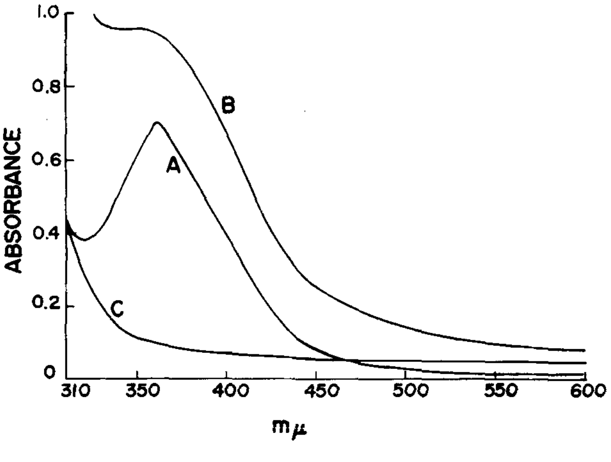

FIG. 1. Spectra of treated and untreated oils extracted by HAW: A, untreated oil diluted 1000-fold; B, treated without $FeCl_3$ and diluted 10-fold; C, treated with $FeCl_3$ and diluted 10-fold.

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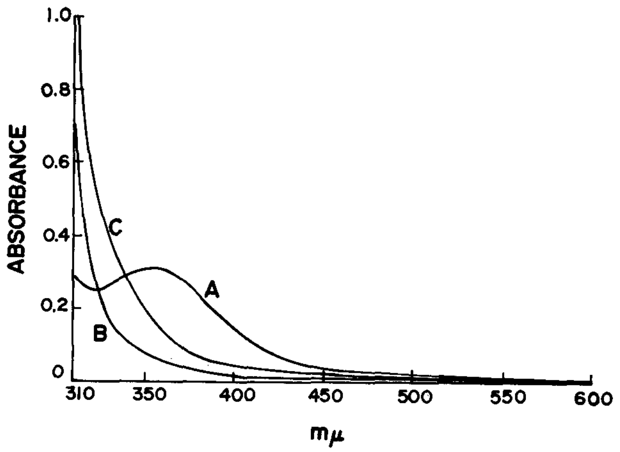

FIG. 2. Spectra of treated and untreated oils extracted by hexane and spectrum of commercial cottonseed oil: A, untreated oil diluted 50-fold; B, treated with or without $FeCl_3$ and diluted five-fold; C, commercial oil diluted five-fold.

steps are involved: formation of an iron-gossypol complex (7), and manipulation of the complex for its removal.

The first step occurs upon the simple addition of ferric chloride to the miscella. However, the mere passage of this treated miscella through natural earth does not remove the pigments, even when the miscella is washed with water.

Washing the treated miscella with an alkaline solution removes free fatty acids (Table I) and some pigmented material by partitioning and precipitation, but more important, this treatment enabled subsequent removal of pigmented material from the oil by passage through natural bleaching earth.

TABLE I

Absorbance and Free Fatty Acid Content of Undiluted Oils Before and After Treatment and of Commercial Cottonseed Oil

Sample	Absorbance at 360 mμ	Relative absorbance	Free fatty acid, %
HAW, untreated	700.00	1076.90	3.94
HAW, treated without $FeCl_3$	9.60	14.80	......
HAW, treated with $FeCl_3$	1.00	1.54	0.07
Hexane, untreated	15.75	24.30	0.72
Hexane, treated without $FeCl_3$	0.28	0.43	......
Hexane, treated with $FeCl_3$	0.28	0.43	0.61
Commercial oil	0.65	1.00	0.04

Although commercial application of this method might produce some problems, e.g., removal of natural antioxidants, much of the oil currently regarded as color-fixed might well be recovered by this method. In preliminary experiments, several color-fixed oils, even an oil that remained colored after commercial processing, were decolorized. Furthermore, since commercial processing of oil involves treatment with alkali and clay already, perhaps addition of ferric ions to the miscella under present conditions will be sufficient for decolorization and reclamation of most of the cottonseed oil produced in the United States.

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