Desorption of Soy Oil Lutein from Rice Hull Cristobalite with Polar Solvents

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The effectiveness of sequential isopropanol/hexane washes of increasing polarity for desorbing soy oil pigment (lutein) from alkaline and acid rice hull ash was studied. Increasing the polarity promoted desorption of pigment. However, the amount of pigment desorbed with each extraction decreased after washing with 2% isopropanol. More lutein was desorbed as the amount of adsorbed lutein increased. Desorption from acid ash was greater than that from alkaline ash, which may be due to the absence of potassium from acid ash. The data suggest that the adsorption sites, occupied by lutein, are not all equally accessible to isopropanol, probably because of the irregular structure of the ash.

KEY WORDS: Cristobalite, desorption, isopropanol, lutein, rice hull ash, soy oil.

The commercial bleaching of soy oil is important for producing a light-colored oil that is acceptable to consumers, and is done by removing the carotenoid lutein, the major pigment in soy oil. Bleaching is achieved by adsorption of oil pigments onto bleaching clay at 100°C under reduced pressure (1). However, studies with model systems have shown that the pigments of cottonseed (2) and soybean (3) oils also can be removed at ambient temperatures and pressures from oil/hexane miscellas by bleaching clays (2) and silicic acid (4).

The adsorption of lutein by silicic acid is reversible and is inhibited by the addition of polar solvents, such as isopropanol (IPA). Proctor and Snyder (4) suggested that IPA competes with lutein for adsorption sites on silicic acid. This competition is based, at least in part, on solvent polarity. Soy lutein can be desorbed from silicic acid by washing the adsorbent with successive volumes of IPA in hexane of increasing polarity (5). The silicic acid was capable of adsorbing soy lutein after desorption.

More recently, rice hull ash, consisting almost exclusively of cristobalite, has been shown to adsorb lutein from soy oil in the same way silicic acid does (3,6). The objective of this study was to observe the degree to which lutein can be desorbed from rice hull cristobalite by extraction with IPA.

MATERIALS AND METHODS

Oil, solvents and adsorbents. Commercial crude soybean oil (Karlshamns Food Ingredients, Columbus, OH) stored at 4°C was used throughout the study. Solvents were reagent grade. Alkaline ash adsorbent was prepared by removing carbon from commercially produced rice hull ash (Riviana Foods, Houston, TX) by heating at 500°C, according to the method of Proctor and Palaniappan (3). Acid ash adsorbent was prepared from alkaline ash adsorbent by sequentially washing with sulfuric acid and water (3).

Lutein measurement. Pigment concentration was determined by the method of Proctor and Snyder (4,5), based on absorbance at 445 nm.

Lutein desorption. This was done according to the method of Proctor and Snyder (5). One-gram quantities of either acid or alkaline ash were mixed with 100 mL of 10%, 20%, 30% or 40% commercial crude soy oil in hexane (w/v) miscellas for 15 min. The amount of pigment adsorbed was measured by the difference in lutein concentration of the miscella before and after the addition of ash. The adsorbent was recovered, washed in excess hexane to remove residual oil, and dried in an air oven at 100°C to remove the solvent. When the recovered adsorbent was dry, it was immediately subjected to 100-mL sequential washes of 0.75%, 2%, 4%, and 8% IPA in hexane (v/v) (5). During each wash, the ash and solvent were continuously stirred in a sealed vessel for 15 min. The amount of lutein desorbed was measured after each wash treatment, and is expressed as μmoles of lutein and as the percentage of adsorbed lutein (5).

RESULTS AND DISCUSSION

Figure 1 shows the effectiveness of sequential washes with IPA in hexane of increasing polarity in promoting desorption of lutein from alkaline rice hull ash, previously exposed to soy oil in hexane miscellas of varying oil concentrations. An increasing amount of pigment was released from alkaline rice hull ash by sequential washings with 0.75, 2, and 4% IPA. The 2% IPA wash was the most effective solvent for desorbing the pigment from alkaline rice hull ash. Each of the successive washes desorbed progressively smaller quantities of lutein; the final wash

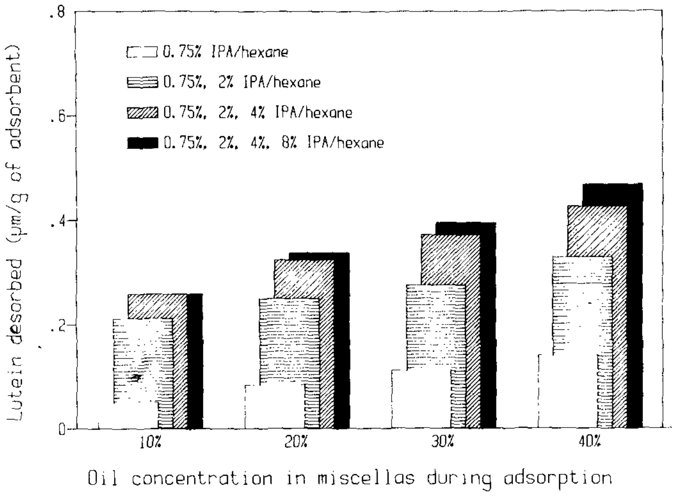

FIG. 1. Lutein desorbed from 1-g amounts of alkaline rice hull ash previously stirred with 100 mL of 10%, 20%, 30% or 40% soy oil/hexane miscellas. Lutein was desorbed by sequential washes of isopropanol (IPA)/hexane. Each extraction was administrated as a 100-mL volume. Lutein was measured by absorbance at 445 nm at 22°C.

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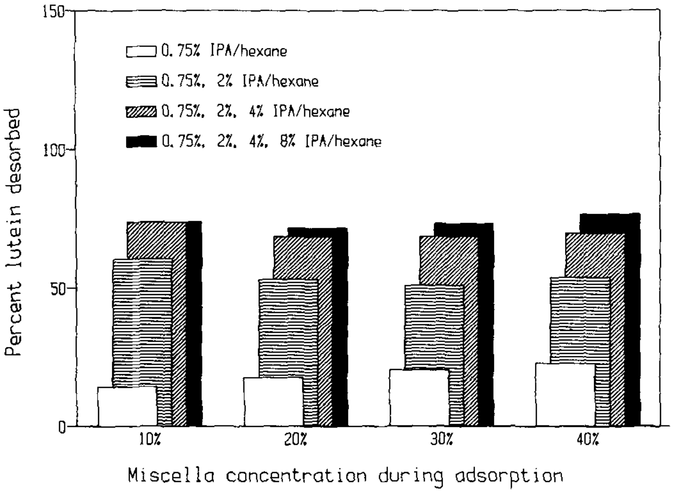

FIG. 2. Percentage of lutein desorbed (molar basis) from 1-g amounts of alkaline rice hull ash previously stirred with 100 mL of 10%, 20%, 30% or 40% soy oil/hexane miscellas. Lutein desorbed by isopropanol (IPA)/hexane sequences is expressed as a percentage of the pigment originally adsorbed. Each extraction was administrated as a 100-mL volume. Lutein was measured by absorbance at 445 nm at 22°C.

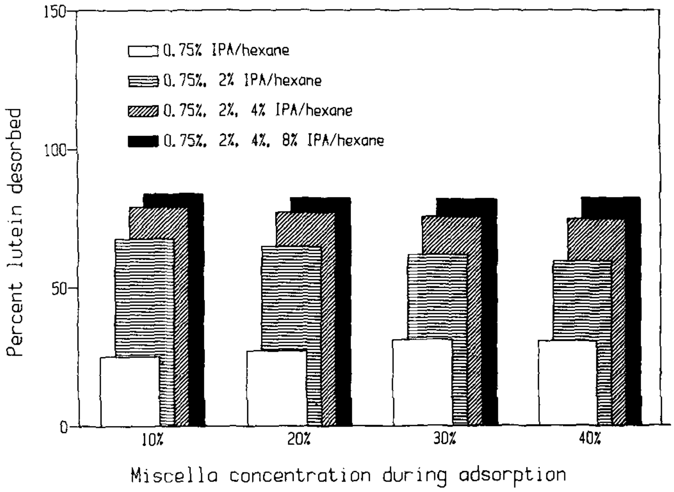

FIG. 4. Percentage of lutein desorbed (molar basis) from 1-g amounts of acid rice hull ash previously stirred with 100 mL of 10%, 20%, 30% or 40% soy oil miscellas. Isopropanol (IPA)/hexane sequences are expressed as a percentage of the pigment adsorbed. Each extraction was administrated as a 100-mL volume. Lutein was measured by absorbance at 445 nm at 22°C.

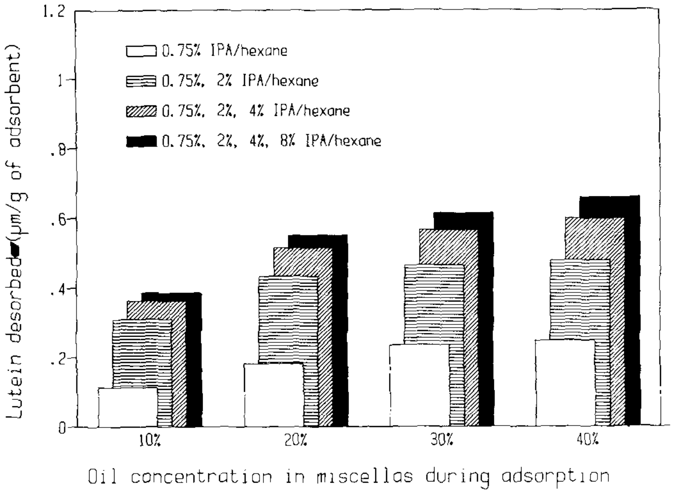

FIG. 3. Lutein desorbed from 1-g amounts of acid rice hull ash previously stirred with 100 mL of 10%, 20%, 30% or 40% soy oil/hexane miscellas. Lutein was desorbed by sequential washes of isopropanol (IPA)/hexane. Each extraction was administrated as a 100-mL volume. Lutein was measured by absorbance at 445 nm at 22°C.

with 8% IPA was the least effective. The amount of pigment desorbed increased with original miscella concentration because more pigment was adsorbed from the more concentrated miscellas.

Figure 2 shows the amount of lutein desorbed from alkaline ash expressed as a proportion of the originally bound pigment. The desorption patterns were similar to those expressed on a molar basis (Fig. 1). In every case about 20% of the adsorbed lutein remained bound after the final elution. For each wash, there may be an equilibrium between bound and free pigment. The ratio of bound to free lutein, after adsorption, would then be the same regardless of the amount of pigment initially bound.

Figure 3 shows the effectiveness of sequential washes with increasing IPA concentrations for desorbing lutein from acid rice hull ash, which has been previously exposed to miscellas of varying soy oil concentrations. The pattern of pigment elution from acid ash was similar to that from alkaline ash. However, more lutein was desorbed from acid rice hull ash for each solvent extraction than from alkaline ash.

Figure 4 shows the amount of lutein desorbed from acid ash as a proportion of the lutein originally bound. The proportion of lutein desorbed, for each wash, was largely independent of miscella concentration, as was observed with alkaline ash. However, a greater proportion of bound pigment was desorbed from acid ash than from alkaline ash (Fig. 2).

The reduced desorption of lutein from alkaline ash relative to acid ash could be due to the presence of potassium ions in alkaline ash and its absence from acid ash (7). In bleaching clays, interaction with metal cations increases the ionic nature of lutein, making it more readily absorbed and less readily desorbed (8). However, adsorption of lutein by acid ash is exclusively by hydrogen bonding to silanol groups, and IPA may readily compete with lutein for adsorption sites on the basis of polarity, as is the case with silicic acid. In addition, acid ash particle size is slightly smaller than that of alkaline ash, which may further facilitate lutein desorption by IPA/hexane.

Proctor and Snyder (5) suggested that lutein desorbed from silica by increasing solvent polarity may represent pigment bound at adsorption sites that are increasingly inaccessible. These sites may be in cracks and crevices in the adsorbent particles (5). This hypothesis would also apply to rice hull ash whose structure is more irregular and heterogeneous than silicic acid (7). Therefore, there may be more "difficult to reach" sites, which may explain why lutein desorption from rice hull ash occurs less readily than from silicic acid (5).

These findings may have some significance in the recycling of adsorbent for ambient-temperature refining of soy oils. The lack of ash particle uniformity relative to synthetic silicic acid may limit the ability of the ash to desorb soy lutein. This effect may be overcome by reducing the particle size. Similarly, the presence of cations may inhibit desorption. Future studies will investigate the effect of ash particle size on adsorption/desorption and the production of a finer, more uniform adsorbent.

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